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UNITED STATES
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J. A. KRUG, SECRETARY

BUREAU OF MINES
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INFORMATION CIRCULAR

UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS

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BY

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS[1]

By Harold M. Smith[2] and W. C. Holliman[3]

Among the more important raw materials now utilized for the commercial production of synthetic organic chemicals is natural gas. Natural gas has been used as a fuel and source of energy almost from its discovery, but its potentialities as a chemical raw material were not realized until recently.

Research in the use of natural gas for chemical synthesis received great impetus from the discovery by Brooks and Humphrey[4] in 1918 of alcohols in the diluted "acid oil" obtained by sulfuric acid treatment of cracked petroleum distillates. Experimental data soon showed that hydrocarbons from natural gas could be converted to these same products. Laboratory methods for chlorination of natural-gas hydrocarbons, particularly of methane for the production of methyl chloride, methylene chloride, carbon tetrachloride, and chloroform were known before that time but were not developed commercially. Methods for obtaining alcohol by oxidation of hydrocarbons derived from natural gas also were known before 1918 but had not received commercial consideration. Since 1918, and particularly during the past 15 years, the work of chemists and chemical manufacturers throughout the world has resulted in an accumulation of data regarding the reactivity of natural-gas hydrocarbons, and related hydrocarbons found in refinery gases or made synthetically. These data have been used to develop methods for converting hydrocarbons into chemical products and thus form the basis for a large and growing industry.

Wartime demands for chemicals during 1939-1945 gave impetus to this development, especially to the application of engineering technology to methods already known in the laboratory but which had not been developed commercially. The production of plastics as substitutes for rubber and silk; of ammonia, glycerine, toluene, and nitroparaffins for use in explosives; of synthetic rubber; and of aviation gasoline are examples of this technologic growth. The demand for these products required new sources of raw materials, and as a result many processes were developed and plants constructed to utilize natural gas and other petroleum hydrocarbons. With the cessation of hostilities, the conversion of these plants and processes to peacetime activities has been rapid. Additional postwar construction of plants for chemical utilization of petroleum gases indicates that the growth of this phase of the petroleum industry will continue.

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[1] The Bureau of Mines will welcome reprinting of this paper provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7347."

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[4] Brooks, B. T., and Humphrey, I., The Action of Concentrated Sulfuric Acid on Olefins with Particular Reference to the Refining of Petroleum Distillates: Jour. Amer. Chem. Soc., vol. 40, 1918, pp. 822-856.

The quantity of natural gas that is, or that under present demands can be utilized in the production of chemicals is not great in comparison with the amount used as fuel. Some data showing present consumption of natural gas for several purposes are presented and discussed with chart 2. Generally, an organic chemical product can be made from any one of several starting materials as well as by several routes from a single substance. This is illustrated by and discussed with chart 5. This versatility of hydrocarbon conversion processes is important, as ordinarily it may be assumed that a substance will not be made synthetically from naturally occurring raw materials if it can be obtained in sufficient quantities as a byproduct from an active commercial process. The cheapness and availability of natural gas, however, has caused unusual consideration to be given to its chemical utilization. Many chemicals not previously procurable commercially have been made from natural-gas hydrocarbons, and in many instances they have filled needs that had not been met by other known substances.

The production, from natural gas, of aviation gasoline and of high anti-knock blending agents for enrichment of motor fuels is not strictly a "utilization for chemical products." Many of these gasoline components, however, are relatively pure chemicals, and the processes employed in their manufacture are applicable to the manufacture of products intended for chemical rather than energy uses. Investigations of production of motor fuels from natural gas and refinery byproduct gases, which were begun actively about 1928, resulted in the discovery of many processes. These investigations also disclosed additional methods and technology for production of pure chemicals and chemical raw materials from natural-gas hydrocarbons. A report giving the results of some of the early investigations of this problem by the Bureau of Mines were published in October 1931.5/ In that report, previous and concurrent work by other investigators is cited.

An information circular concerning the utilization of natural gas for chemical products was published by the Bureau in 1930.6/ and a revision was issued in 1940.7/ The present paper is a revision of the 1940 publication. Its purpose is to show in graphic form the general reactions used and the chemical products that may be obtained when natural gas is used as a raw material. The number of products presently obtainable from natural gas is very large, and the field is continuing to develop, so that it is possible that some products that are now important (or soon may be so) have been omitted, but every effort has been made to make this publication as inclusive as available information permits. The products listed may be

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5/ Smith, H. M., Grandone, Peter, and Rall, H. T., The Production of Motor Fuels from Natural Gas: Bureau of Mines Rept. of Investigations 3143, 1931, 12 pp.

6/ Smith, Harold M., Possible Use of Natural Gas for the Production of Chemical Products: Bureau of Mines Inf. Circ. 6388, 1930, 5 pp.

7/ Smith, Harold M., Utilization of Natural Gas for Chemical Products: Bureau of Mines Inf. Circ. 7108, 1940, 18 pp.

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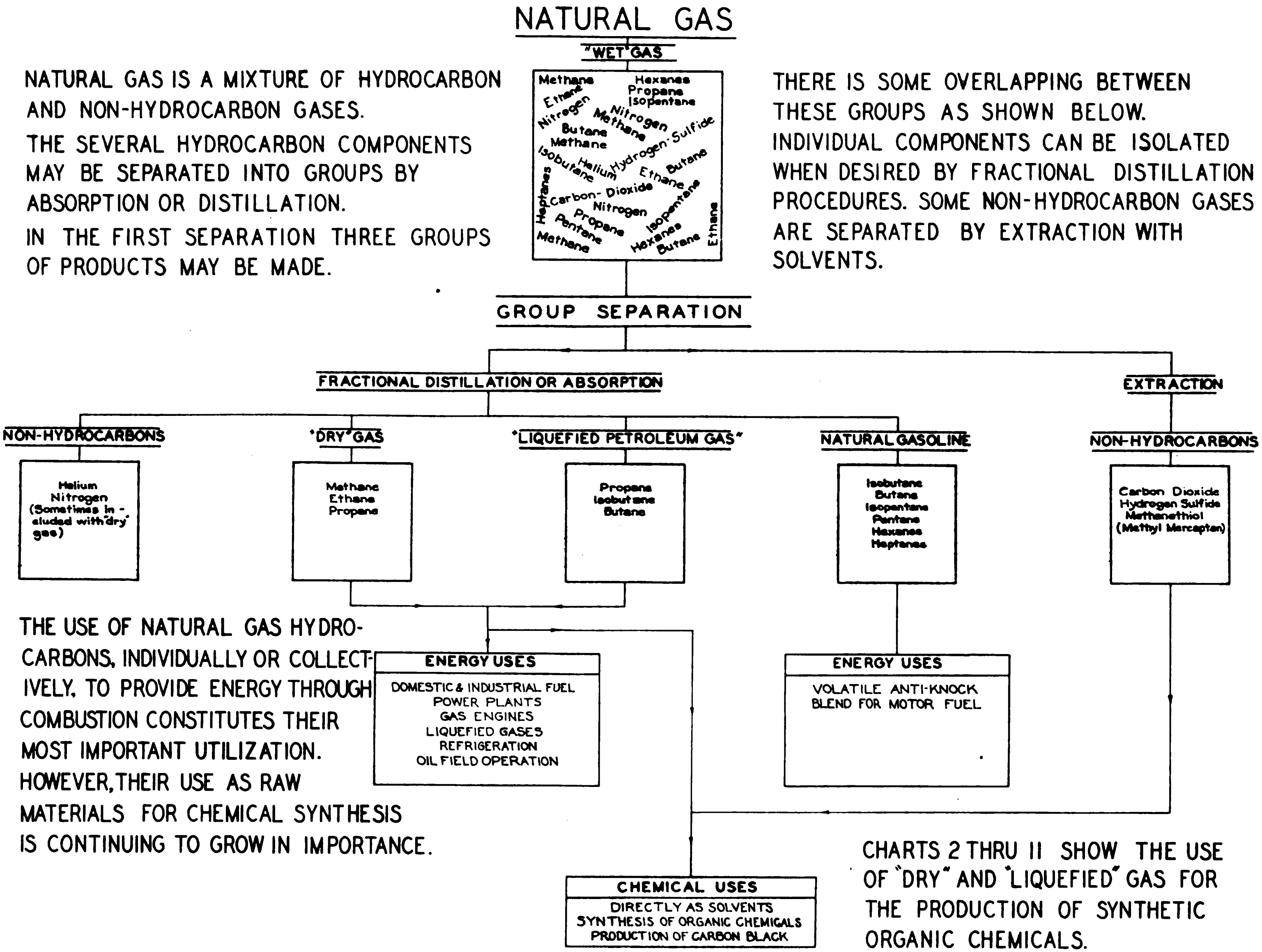
CHART I

NATURAL GAS IS A MIXTURE OF HYDROCARBON AND NON-HYDROCARBON GASES.

THE SEVERAL HYDROCARBON COMPONENTS MAY BE SEPARATED INTO GROUPS BY ABSORPTION OR DISTILLATION.

IN THE FIRST SEPARATION THREE GROUPS OF PRODUCTS MAY BE MADE.

THERE IS SOME OVERLAPPING BETWEEN THESE GROUPS AS SHOWN BELOW. INDIVIDUAL COMPONENTS CAN BE ISOLATED WHEN DESIRED BY FRACTIONAL DISTILLATION PROCEDURES. SOME NON-HYDROCARBON GASES ARE SEPARATED BY EXTRACTION WITH SOLVENTS.



THE USE OF NATURAL GAS HYDROCARBONS, INDIVIDUALLY OR COLLECTIVELY, TO PROVIDE ENERGY THROUGH COMBUSTION CONSTITUTES THEIR MOST IMPORTANT UTILIZATION. HOWEVER, THEIR USE AS RAW MATERIALS FOR CHEMICAL SYNTHESIS IS CONTINUING TO GROW IN IMPORTANCE.

CHARTS 2 THRU 11 SHOW THE USE OF "DRY" AND "LIQUEFIED" GAS FOR THE PRODUCTION OF SYNTHETIC ORGANIC CHEMICALS.

produced from natural gas from wells or natural gasoline plants, but ordinarily natural gas would not be used where refinery-process gases or other raw materials are available that will yield the desired product in fewer steps and more cheaply. Some statistics relating to the economics and growth of the industry are shown in the first charts, and the principal processes and their products are shown in the others.

It would be desirable to include brief descriptions of some of the processes, but choices of methods and operating conditions are so varied that no simple explanation seems possible. Actually, few of the reactions are as simple as the charts may indicate. The subject of catalysts alone is so complex that it cannot be presented adequately in a report such as this. The nontechnical reader is interested mainly in the general picture which is adequately shown by the charts. A selected bibliography is included for the technical reader who may wish to obtain such chemical and engineering information as is generally available and for the nontechnical reader who may wish to inquire further into the subject. Historical and bibliographical reviews of work done in the field have appeared in the literature from time to time, some of which are listed among the references.

Chart 1.

Natural gas is a mixture of gaseous hydrocarbons consisting predominantly of those containing not more than four carbon atoms. It occurs in natural reservoirs separately as gas or may be found with or in solution in nongaseous hydrocarbons. The composition of natural gas may differ from field to field and also with production methods. Methane is the hydrocarbon usually present in greatest volume, with ethane, propane, and heavier hydrocarbons successively next in order. The composition of a "wet" gas typical of much of that produced lies within the following limits in volume percent: Methane, 80-90 percent; ethane, 5-10 percent; propane, 3-5 percent; isobutane and butane, 1-2 percent; pentanes and heavier hydrocarbons, 1-2 percent. Nonhydrocarbon components, including nitrogen, hydrogen sulfide, traces of organic sulfur compounds, carbon dioxide, and helium, may occur with the natural gas. Certain of these may be extracted from natural gas either as impurities or for individual utilization. (Chart 12.)

Chart 1 shows the general composition and major uses of natural gas. The gaseous mixture or "wet" gas produced at the wellhead, as shown in the top square of the chart, usually is separated in the field in absorption or natural-gasoline plants. Nonhydrocarbons are removed under certain conditions, and the hydrocarbons are separated into "dry gas," "liquefied petroleum gas" (sometimes referred to as LPG), and natural gasoline or condensate. ("Dry" gas occurs as such in some fields. When gas is produced with crude oil, a rough field separation gives a wet gas.) Such separations are not ordinarily complete, and there is some overlapping between the groups. Further group separation or separation into individual components is accomplished when desired by fractional distillation, or in special cases by extractive distillation, azeotropic distillation, superfractionation, or other extractive methods.

Data regarding uses of the several constituents are shown in chart 2. Charts 7 to 11, which show chemical products, are concerned primarily with "dry" and "liquefied petroleum gases" hydrocarbons - methane, ethane, propane, isobutane, and n-butane.

Chart 2

Some data regarding the consumption and use of natural and liquefied petroleum gas are shown graphically in charts 2a and 2b. Unfortunately, figures for the quantity of natural gas used in the manufacture of synthetic organic chemicals are not available separately but are included under "other industrial" uses. Data on the use of liquefied petroleum gases in the manufacture of synthetic rubber components were available for the first time in 1944. Data concerning the use of liquefied petroleum gas in the production of aviation gasoline and other motor-fuel components are not included. Chart 2c shows annual synthetic production from all sources of certain non-coal-tar chemicals since 1936. Chart 2d shows the increase in total production and sales of non-coal-tar synthetic organic chemicals from 1925 to 1944 and production and sales of chemicals raw materials derived from petroleum from 1942 to 1944.

Statistics showing the portion of this production using natural gas as the raw material are not available.

Chart 3

Chart 3 shows the general composition of crude petroleum and of refinery-processed petroleum and also lists some nonpetroleum materials suitable for hydrocarbon synthesis. Petroleum is an extremely complex mixture of hydrocarbons and other substances that is found in nature in the solid, liquid, and gaseous states. Natural gas is a form of petroleum that consists of hydrocarbons and other substances (chart 1) that exists in the gaseous state under ordinary conditions of temperature and pressure at the earth's surface. The natural-gas hydrocarbons frequently occur in solution with crude oil. Hydrocarbons identical with those in natural gas, together with unsaturated gaseous hydrocarbons, are formed as byproducts in refinery operations during the manufacture of petroluem products, by decomposition and conversion of natural gas, natural gasoline, or crude-oil hydrocarbons. Such hydrocarbons also may be made synthetically from nonpetroleum materials. These gaseous products, regardless of source, are important raw materials or intermediates for chemical products. The fact that the gaseous products of petroleum may be obtained by processing the heavier fractions and, similarly, that heavier hydrocarbons may be made from the gases is significant. Methods whereby such interconversion of petroleum hydrocarbons can be accomplished are presented in the next chart.

Chart 4

Raw materials other than petroleum hydrocarbons were used for the first commercial syntheses of organic chemicals. The processes, however,

CHART 2

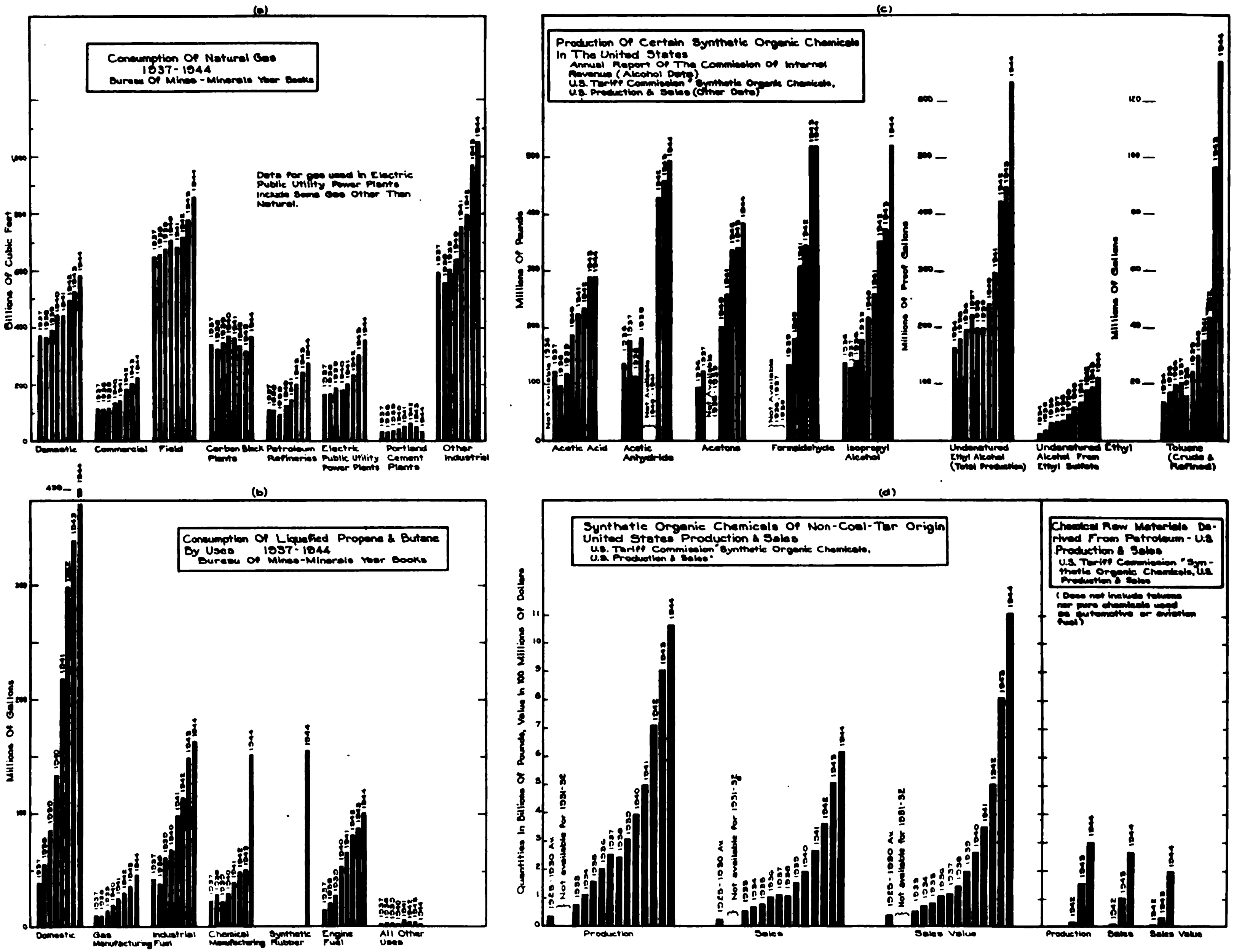

(a)
Consumption Of Natural Gas
1937-1944
Bureau Of Mines - Minerals Year Books
Billions Of Cubic Feet
0
200
400
600
800
1,000
Data for gas used in Electric Public Utility Power Plants include Some Gas Other Than Natural.
Domestic
Commercial
Field
Carbon Black Plants
Petroleum Refineries
Electric Public Utility Power Plants
Portland Cement Plants
Other Industrial
(b)
Consumption Of Liquefied Propane & Butane By Uses 1937-1944
Bureau Of Mines-Minerals Year Books
Millions Of Gallons
0
100
200
300
430
Domestic
Gas Manufacturing
Industrial Fuel
Chemical Manufacturing
Synthetic Rubber
Engine Fuel
All Other Uses
(c)
Production Of Certain Synthetic Organic Chemicals In The United States
Annual Report Of The Commission Of Internal Revenue (Alcohol Data)
U.S. Tariff Commission "Synthetic Organic Chemicals, U.S. Production & Sales (Other Data)
Millions Of Pounds
0
100
200
300
400
500
Not Available 1934
Not Available 1940-1941
Not Available 1936, 1937, 1938
Acetic Acid
Acetic Anhydride
Acetone
Formaldehyde
Isopropyl Alcohol
Millions Of Proof Gallons
100
200
300
400
500
600
Undenatured Ethyl Alcohol (Total Production)
Millions Of Gallons
20
40
60
80
100
120
Undenatured Ethyl Alcohol From Ethyl Sulfate
Toluene (Crude & Refined)
(d)
Synthetic Organic Chemicals Of Non-Coal-Tar Origin
United States Production & Sales
U.S. Tariff Commission "Synthetic Organic Chemicals, U.S. Production & Sales"
Quantities In Billions Of Pounds, Value In 100 Millions Of Dollars
0
1
2
3
4
5
6
7
8
9
10
11
1925-1930 Av.
Not available for 1931-32
Production
Sales
Sales Value
Chemical Raw Materials Derived From Petroleum - U.S. Production & Sales
U.S. Tariff Commission "Synthetic Organic Chemicals, U.S. Production & Sales
(Does not include toluene nor pure chemicals used as automotive or aviation fuel)
Production
Sales
Sales Value

CHART 3

COMPOSITION OF PETROLEUM
RELATIONSHIP AND SOURCES OF PETROLEUM-TYPE HYDROCARBONS

NATURAL GAS

Hydrocarbons
- Methane
- Ethane
- Propane
- Butanes
- Heavier hydrocarbons separated as natural gasoline (CHART 1)

Other constituents
- Nitrogen - Helium
- Carbon dioxide - Sulfur compounds

CRUDE PETROLEUM

Dissolved gaseous hydrocarbons
- Natural gas hydrocarbons (Methane, ethane, propane, butanes)

Liquid hydrocarbons
- Higher molecular weight homologues (pentanes and heavier) of natural gas hydrocarbons, and cyclic compounds

Solid hydrocarbons
- Paraffin waxes, petrolatum, and cyclic compounds

Other constituents
- Asphaltic compounds
- Sulfur compounds

Natural gas may occur separately or coexistent with heavier petroleum hydrocarbons (natural gasoline, condensate, crude petroleum). Crude petroleum frequently contains natural gas hydrocarbons but consists primarily of heavier hydrocarbons.

REFINERY PROCESSED PETROLEUM

Gaseous hydrocarbons

Saturated:	Unsaturated:
Methane	Ethylene
Ethane	Propylene
Propane	Butylenes
Butanes	Butadienes
	Acetylene
	Methylacetylene

Liquid hydrocarbons
- (Gasolines, Kerosine, diesel fuels, lubricating oils).
- Pentanes and higher molecular weight paraffins, naphthenes, unsaturated hydrocarbons, and cyclic compounds.

Solid hydrocarbons
- Paraffin waxes, petrolatum, and cyclic compounds.

Refinery gas contains hydrocarbons identical with those in natural gas and in addition contains unsaturated hydrocarbon gases (ordinarily olefins;- acetylene hydrocarbons are formed under some conditions). These gases are produced in refinery operations during manufacture of petroleum products, by decomposition and conversion of natural gas, natural gasoline or crude petroleum hydrocarbons. Heavier hydrocarbons contained in refinery products, such as fuels and lubricants, are either natural petroleum hydrocarbons, or are products of decomposition or conversion processes applied to petroleum or its fractions (including natural gas), or are mixtures of natural and synthetic products.

NON PETROLEUM MATERIALS USED FOR SYNTHESIS OF HYDROCARBONS

Coal or coke
Limestone
} Calcium carbide

Coal, coke, or other carbonaceous material
Steam or oxygen
} Carbon monoxide and hydrogen

Coal
Lignite
Oil shale
Vegetative materials subject to fermentation or natural decomposition.

Hydrocarbons identical to natural and refinery processed petroleum hydrocarbons may be made synthetically from non-petroleum materials by chemical methods (Fischer-Tropsch synthesis, hydrogenation of coal, reaction of calcium carbide and water), or obtained from vegetative materials subject to fermentation, or from other carbonaceous materials or materials containing organic matter, such as oil shale.

CHART 4

METHODS FOR CONVERSION OF PETROLEUM HYDROCARBONS
DIRECTLY OR INDIRECTLY APPLICABLE TO NATURAL GAS

These definitions of methods of converting hydrocarbons conform to the apparent general usage of the terms in the literature of the petroleum industry.

1. DECOMPOSITION (thermal, catalytic, electric): The splitting of the hydrocarbon molecule into smaller molecules or into carbon and hydrogen by heat alone (pyrolysis), with the aid of catalysts, or by electric discharge. Generally accompanied, especially in pyrolysis, by recombination of some of the products into new compounds.

$$\underset{C_2H_6}{\text{Ethane}} \xrightarrow[\text{or electric arc}]{\text{heat, catalyst}} \underset{H_2}{\text{Hydrogen}} + \underset{C_2H_4}{\text{Ethylene}}$$

$$\underset{C_2H_6}{\text{Ethane}} \xrightarrow[\text{heat, catalyst}]{\text{electric arc or}} \underset{2H_2}{\text{Hydrogen}} + \underset{C_2H_2}{\text{Acetylene}}$$

$$\underset{C_2H_6}{\text{Ethane}} \xrightarrow[\text{decomposition)}]{\text{(maximum}} \underset{3H_2}{\text{Hydrogen}} + \underset{2C}{\text{Carbon}}$$

2. OXIDATION (thermal, catalytic): Reaction of the hydrocarbon molecule with oxygen, air or oxygen-containing compounds, activated by heat or catalyst, whereby oxygen is introduced into the hydrocarbon molecule, or the molecule is changed to carbon monoxide and hydrogen, carbon dioxide and hydrogen, or finally to carbon dioxide and water.

$$\underset{2C_2H_6}{\text{Ethane}} + \underset{O_2}{\text{Oxygen}} \xrightarrow[\text{catalyst}]{\text{heat \& pressure}} \underset{2C_2H_5OH}{\text{Ethyl alcohol}}$$

$$\underset{C_2H_6}{\text{Ethane}} + \underset{4H_2O}{\text{Water(Steam)}} \xrightarrow[\text{catalyst}]{\text{heat and}} \underset{7H_2}{\text{Hydrogen}} + \underset{2CO_2}{\text{Carbon dioxide}}$$

$$\underset{C_2H_6}{\text{Ethane}} \xrightarrow[\text{oxidation)}]{\text{(maximum}} \underset{3H_2O}{\text{Water}} + \underset{2CO_2}{\text{Carbon dioxide}}$$

3. HALOGENATION (thermal, catalytic, photolytic): Reaction of the hydrocarbon molecule with a halogen (fluorine, chlorine, bromine, iodine), activated by heat, light, or catalyst, whereby one or more halogen atoms replace an equivalent number of hydrogen atoms in the hydrocarbon molecule.

$$\underset{C_2H_6}{\text{Ethane}} + \underset{Cl_2}{\text{Chlorine}} \xrightarrow[\text{or catalyst}]{\text{heat, light}} \underset{C_2H_5Cl}{\text{Ethyl chloride}} + \underset{HCl}{\text{Hydrogen chloride}}$$

4. NITRATION (thermal, vapor phase): Reaction of the hydrocarbon molecule with nitric acid, accelerated by heat and pressure, whereby a nitro group, NO_2, is introduced into the hydrocarbon by replacing a hydrogen atom.

$$\underset{C_2H_6}{\text{Ethane}} + \underset{HNO_3}{\text{Nitric acid}} \xrightarrow{\text{(vapor phase)}} \underset{C_2H_5NO_2}{\text{Nitroethane}} + \underset{H_2O}{\text{Water}}$$

5. SULFURIZATION: Reaction of the hydrocarbon molecule with sulfur or hydrogen sulfide to form sulfur-containing compounds such as organic sulfides, mercaptans, disulfides, thiophenes

$$\underset{C_2H_6}{\text{Ethane}} + \underset{S}{\text{Sulfur}} \xrightarrow{\text{catalyst}} \underset{C_2H_5SH}{\text{Ethyl mercaptan}}$$

6. DESULFURIZATION (catalytic): Removal of the sulfur atom from a sulfur-carbon-hydrogen molecule to form a sulfur-free molecule. Activated by catalyst.

$$\underset{C_2H_5SH}{\text{Ethyl mercaptan}} + \underset{H_2}{\text{Hydrogen}} \xrightarrow[\text{and heat}]{\text{catalyst}} \underset{C_2H_6}{\text{Ethane}} + \underset{H_2S}{\text{Hydrogen sulfide}}$$

$$\underset{C_2H_5SH}{\text{Ethyl mercaptan}} \xrightarrow[\text{heat}]{\text{catalyst and}} \underset{C_2H_4}{\text{Ethylene}} + \underset{H_2S}{\text{Hydrogen sulfide}}$$

7. HYDROGENATION (catalytic, thermal catalytic): Addition of hydrogen atoms to an unsaturated hydrocarbon molecule to produce one or more saturated molecules. Activated by catalyst or heat and catalyst. Known as destructive hydrogenation when original unsaturated molecule is "cracked" to form more than one subsequently hydrogenated smaller molecule, or non-destructive when no cracking occurs.

a. Destructive:

$$\underset{C_5H_{12}}{\text{Pentene}} + \underset{H_2}{\text{Hydrogen}} \xrightarrow[\text{catalyst}]{\text{heat and}} \underset{C_3H_8}{\text{Propane}} + \underset{C_2H_6}{\text{Ethane}}$$

b. Non-destructive:

$$\underset{C_2H_4}{\text{Ethylene}} + \underset{H_2}{\text{Hydrogen}} \xrightarrow{\text{catalyst}} \underset{C_2H_6}{\text{Ethane}}$$

8. DEHYDROGENATION (catalytic, thermal): A form of controlled decomposition whereby hydrogen atoms are removed from hydrocarbon molecules to form less highly saturated molecules. Known as destructive dehydrogenation when original molecule is "cracked" to form more than one smaller molecule, or non-destructive when no breaking of carbon-carbon bonds occur.

a. Destructive:

$$\underset{C_5H_{12}}{\text{Pentane}} \xrightarrow[\text{catalyst}]{\text{heat or}} \underset{C_3H_6}{\text{Propylene}} + \underset{C_2H_4}{\text{Ethylene}} + \underset{H_2}{\text{Hydrogen}}$$

b. Non-destructive:

$$\underset{C_2H_6}{\text{Ethane}} \xrightarrow[\text{catalyst}]{\text{heat or}} \underset{C_2H_4}{\text{Ethylene}} + \underset{H_2}{\text{Hydrogen}}$$

9. ALKYLATION (thermal, catalytic): Chemical union of an alkyl radical to a hydrocarbon molecule. Used particularly to designate combination of olefin and isoparaffin or aromatic under conditions of high temperature or in presence of a catalyst.

$$\underset{C_2H_4}{\text{Ethylene}} + \underset{C_4H_{10}}{\text{Isobutane}} \xrightarrow{\text{heat}} \underset{C_6H_{14}}{\text{Neohexane (2,2 dimethyl butane)}}$$

$$\underset{C_4H_8}{\text{Butylene}} + \underset{C_4H_{10}}{\text{Isobutane}} \xrightarrow{\text{catalyst}} \underset{C_8H_{18}}{\text{Isomeric octanes (alkylate)}}$$

$$\underset{C_6H_6}{\text{Benzene}} + \underset{C_3H_6}{\text{Propylene}} \xrightarrow{\text{catalyst}} \underset{C_6H_5CH(CH_3)_2}{\text{Isopropyl benzene (cumene)}}$$

10. POLYMERIZATION (thermal, catalytic): Combination of like molecules (selective) or unlike molecules (non-selective) into chain molecules of higher molecular weight.

a. Selective:

$$\underset{nC_2H_4}{\text{Ethylene}} \longrightarrow \underset{(C_2H_4)_n}{\text{Polyethylene}}$$

b. Non-selective:

$$\underset{C_3H_6}{\text{Propylene}} + \underset{C_5H_{10}}{\text{Amylene}} \longrightarrow \underset{C_8H_{16}}{\text{Mixed octylenes}}$$

11. ISOMERIZATION (thermal, catalytic): Transformation of the molecular structure of a hydrocarbon molecule without changing the empirical composition or molecular weight.

$$\underset{CH_3CH_2CH_2CH_3}{\text{Butane}} \xrightarrow{\text{catalyst}} \underset{\substack{CH_3-CH-CH_3\\ |\\ CH_3}}{\text{Isobutane}}$$

12. CYCLIZATION and AROMATIZATION (thermal, catalytic): Conversion of paraffinic or naphthenic hydrocarbon molecules to cyclic and aromatic molecules. Accompanied by dehydrogenation and by prior polymerization in some cases as where gaseous hydrocarbons are used as raw material.

$$\underset{C_6H_{14}}{\text{Hexane}} \xrightarrow{\text{catalyst}} \underset{C_6H_{12}}{\text{Cyclohexane}} + \underset{H_2}{\text{Hydrogen}}$$

$$\underset{C_6H_{12}}{\text{Cyclohexane}} \xrightarrow{\text{catalyst}} \underset{C_6H_6}{\text{Benzene}} + \underset{3H_2}{\text{Hydrogen}}$$

13. HYDROCARBON SYNTHESIS: Hydrocarbons identical with those from petroleum may be formed from organic or inorganic materials by synthetic processes such as Fischer-Tropsch synthesis or action of water on calcium carbide.

$$\underset{nCO+(2n+1)H_2}{\text{Synthesis gas}} \xrightarrow[\text{Reaction (catalytic)}]{\text{Fischer-Tropsch}} \text{Straight chain paraffin } \underset{C_nH_{2n+2}}{\text{hydrocarbons}} + \underset{nH_2O}{\text{Water}}$$

$$\underset{CaC_2}{\text{Calcium carbide}} + \underset{2H_2O}{\text{Water}} \longrightarrow \underset{Ca(OH)_2}{\text{Calcium hydroxide}} + \underset{C_2H_2}{\text{Acetylene}}$$

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usually involved as a first step hydrogenation of carbon or formation of hydrogen-carbon products similar to those already present in natural gas or easily derived from petroleum. It was soon recognized that petroleum and natural-gas hydrocarbons offer raw materials suitable in their original form, or after rearrangement to new molecular structure, for use in synthesis of chemical products. Further steps in the production of synthetic organic chemicals involve the addition or substitution of other elements such as oxygen, chlorine, nitrogen, or sulfur to the hydrocarbon structure. Typical methods for rearranging the hydrocarbon molecule and for converting it into other products are shown and defined in chart 4.

Probably the most important method used for converting petroleum hydrocarbons to other compounds is decomposition effected by pyrolysis, catalysis, or electric discharge. Decomposition as used here also includes, in many instances, subsequent recombination of primary products into new compounds. Dehydrogenation and hydrogenation, alkylation, polymerization, isomerization, desulfurization, and cyclization and aromatization all may be considered as special cases of controlled decomposition or decomposition and recombination. Some methods of oxidation, halogenation, nitration, sulfurization, and amination involve preliminary decomposition of saturated hydrocarbons to olefins and recombination with the added elements.

Decomposition, oxidation, halogenation, nitration, and sulfurization are further discussed with the charts showing products obtained by use of the respective methods. Many of the products shown on these charts are the result of a second series of reactions or conversions using the primary products as starting materials. Some typical examples of such reactions are shown in chart 4, and the following deserve special mention: Alkylation and hydrogenation have been of especial importance in the production of high anti-knock blending agents for aviation gasoline; isomerization has been used extensively to convert n-butane or n-pentane to isobutane or isopentane for use in alkylation and in aviation gasoline. Selective and nonselective polymerization is used in the manufacture of intermediates for plastics and synthetic rubbers as well as in making motor fuels and lubricants; desulfurization is often a necessary process in the production of motor fuels; dehydrogenation (and sometimes polymerization) together with cyclization and aromatization is used in the production of aromatics and cyclic compounds. The development of processes using these conversion methods received much consideration before and during the recent war, and processes developed are now being adapted to peacetime needs.

It has been mentioned already that coal, petroleum, agricultural products, and other carbonaceous materials may be used interchangeably as raw materials for hydrocarbon synthesis and manufacture of chemicals. Hydrocarbon synthesis and production of chemicals from materials other than petroleum has been used in Germany and in our own country as a wartime measure. Liquid fuels, lubricants, materials for synthetic rubber, and a large number of organic chemicals were produced in Germany from coal (or in some cases natural gas).

Among the processes using coal or coke as raw material are the production of calcium carbide for conversion into acetylene, the hydrogenation of coal to produce gaseous and liquid hydrocarbons, and the Fischer-Tropsch synthesis, which involves a prior oxidation of coal or other carbonaceous material with oxygen or steam. Natural gas may be used in this process instead of coal, and this application has received much interest recently. It is discussed further with the chart showing products obtained by oxidation (chart 8). Similarly, acetylene is produced also by decomposition of natural gas or gas from coal hydrogenation and is discussed further with chart 7.

Chart 5

Chart 5 shows diagrammatically the production of butadiene by several possible methods using some of the possible raw materials. The chart illustrates the diverse routes by which a desired organic chemical may be obtained. Economic considerations involved usually determine the choice of raw materials and route. Butadiene for synthetic rubber was produced from coal in Germany during the war, whereas in America it was made on an extensive scale from ethyl alcohol, which was obtained from agricultural sources, or from petroleum; also, directly from petroleum hydrocarbons, chiefly from butylenes and butanes. The choice of starting material in each instance was determined by the availability and need for the several types of materials. In Germany, coal was the initial raw material, but actual butadiene production was mainly from byproduct gases obtained in the hydrogenation of coal. These gases were converted into acetylene and ethylene by means of the electric arc, and the acetylene was converted to acetaldehyde and then to butadiene by the aldol route.

Chart 6

Chart 6 should be used for reference in studying charts 7 to 12, as it indicates the significance of the several "boxes," brackets, and types of lettering used in them. In chart 6 the terms used have the following meanings:

Primary product. - A product obtained directly by the application of the basic method of conversion indicated in the title of the individual chart.

Preferred source. - Not necessarily the only source, but the material reacting most easily or with the best yields relative to other natural-gas hydrocarbons (see remarks under "Charts 7 to 11 - General").

Direct use. - A use (a) in which no chemical change occurs in the substance, as when it is used as a solvent or anesthetic, or (b) when the substance is completely destroyed, as when used for fuel. The direct uses of secondary products are indicated in brackets.

Secondary product. - A product made from the primary product. Common names of secondary products and their derivatives are indicated in parenthesis. Direct uses are shown in brackets.

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CHART 5

SEVERAL POSSIBLE METHODS BY WHICH BUTADIENE MAY BE PRODUCED

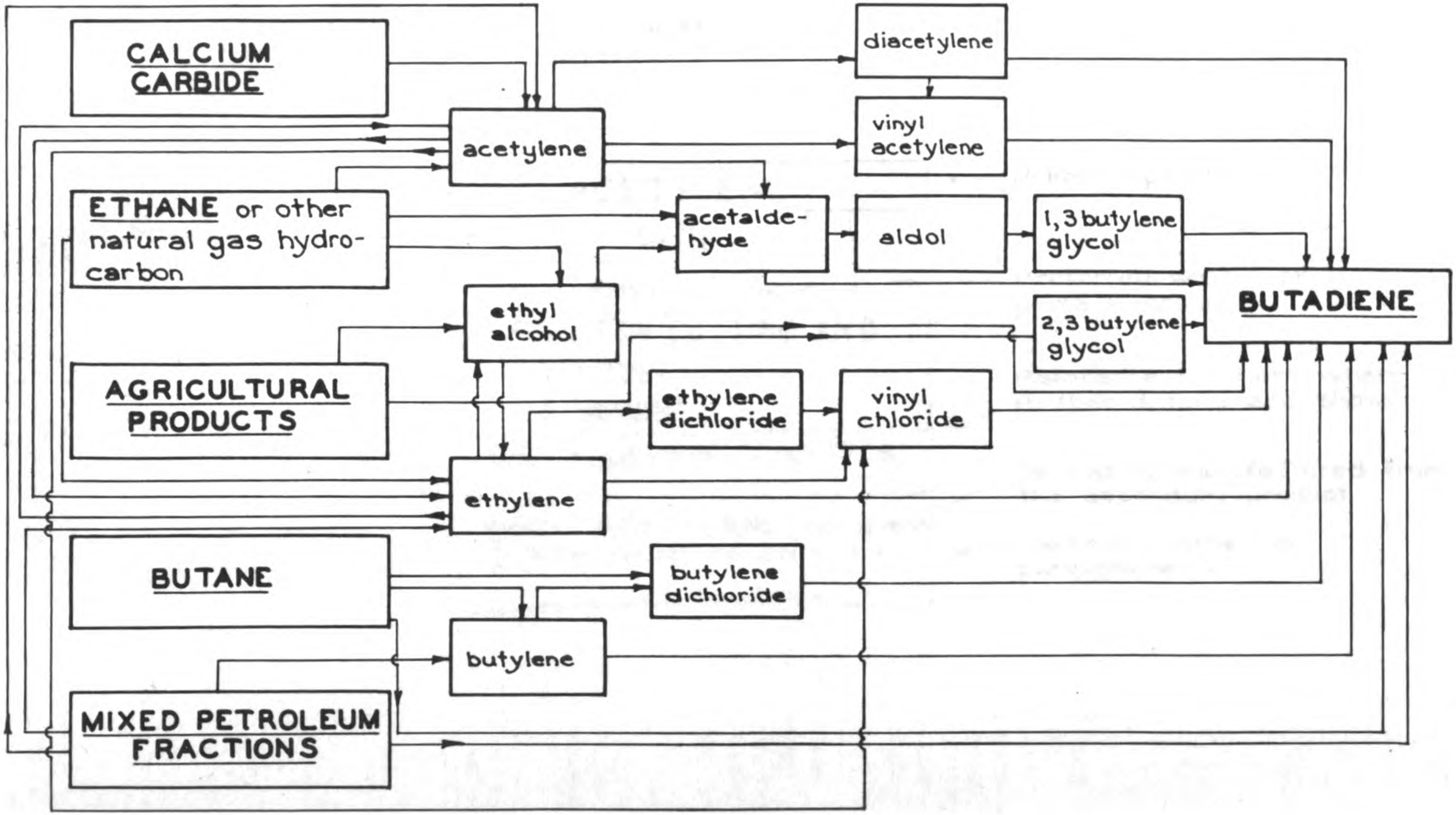

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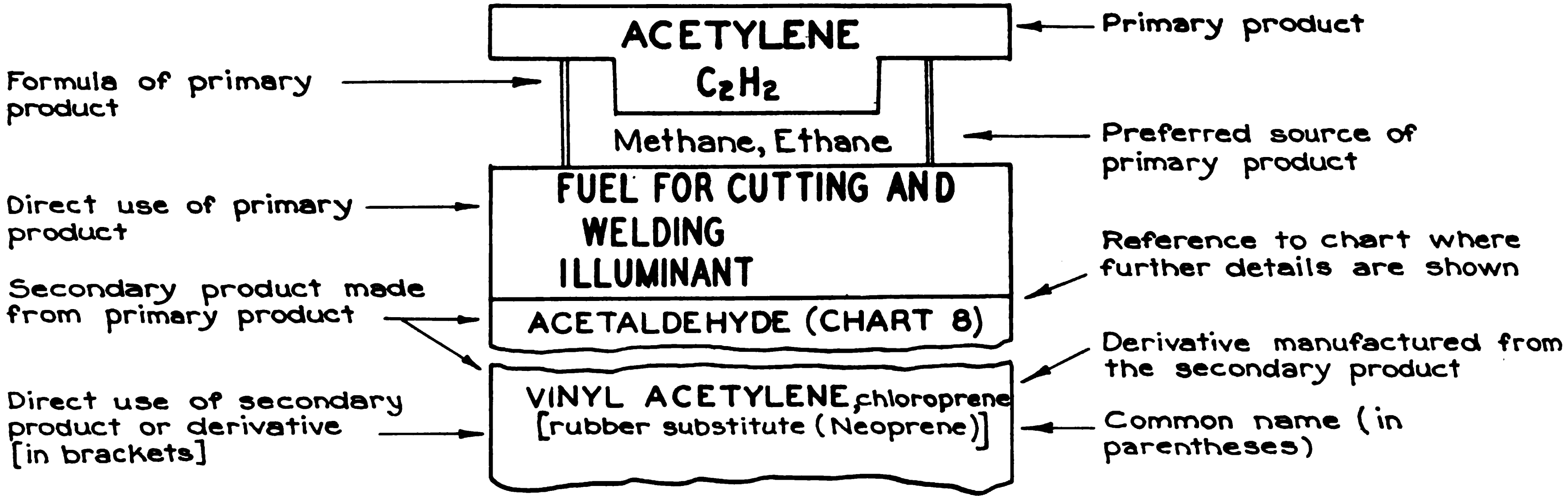
CHART 6


ACETYLENE
C_2H_2
Methane, Ethane
FUEL FOR CUTTING AND WELDING
ILLUMINANT
ACETALDEHYDE (CHART 8)
VINYL ACETYLENE, chloroprene
[rubber substitute (Neoprene)]
Primary product
Formula of primary product
Preferred source of primary product
Direct use of primary product
Reference to chart where further details are shown
Secondary product made from primary product
Derivative manufactured from the secondary product
Direct use of secondary product or derivative [in brackets]
Common name (in parentheses)

Original from THE OHIO STATE UNIVERSITY

CHART 7

PRODUCTS OBTAINABLE FROM NATURAL GAS BY DECOMPOSITION

THERMAL - CATALYTIC - ELECTRIC

GASES

HYDROGEN

H_2

Methane and Heavier Hydrocarbons

FUEL for cutting & welding · INCANDESCENT lamp filler
LIFTING GAS for lighter than air craft
DESULFURIZATION & DEOXYGENIZATION REAGENT

- AMMONIA [refrigerant, fertilizer, nitric acid, ammonium nitrate [explosives and fertilizers], organic amines [solvents, rubber accelerators, dye intermediates], urea [plastics, protein supplement for livestock] nitrides
- HYDROCHLORIC ACID, ANHYDROUS
- HYDROCYANIC ACID
- HYDROGENATED COAL PRODUCTS [motor fuel, aromatics, fuel oil]
- HYDROGENATED PETROLEUM PRODUCTS [aviation gasoline, motor fuels, and lubricants]
- HYDROGENATED VEGETABLE OILS [fats for cooking]
- INTERMEDIATES for nylon type plastics
- SYNTHESIS GAS for Fischer-Tropsch process (CHART 8)

ACETYLENE

C_2H_2

Methane, Ethane

FUEL for cutting & welding
ILLUMINANT

- ACETALDEHYDE (CHART 8)
- ACETIC ACID and ANHYDRIDE (CHART 8)
- ACETONE (CHART 8)
- ACETYLENE BLACK (carbon black)(THIS CHART)
- ACETYLENE HALIDES and POLYHALIDES
- ACETYLIDES
- ACRYLONITRILE (synthetic rubber intermediate)
- AROMATICS
- BUTADIENE (THIS CHART)
- CARBON DISULFIDE (CHART 11)
- FORMIC ACID (CHART 8)
- THIOPHENE (CHART 11)
- VINYL ACETYLENE, chloroprene [rubber substitute (neoprene)]
- VINYL CHLORIDE, VINYL ALCOHOL and VINYL ACETATE, plastics and resins

ETHYLENE

C_2H_4

Methane, Ethane, Propane, Butane, Heavier Hydrocarbons

FUEL for cutting & welding - ANESTHETIC - REFRIGERANT - ACCELERATOR for plant growth & fruit ripening

- ACENAPHTHENE, dyestuff intermediate
- ACETIC ACID and ANHYDRIDE (CHART 8)
- ACETYLENE (THIS CHART)
- ALKYLATES [motor & aviation gasoline]
- ANTHRACENE (THIS CHART)
- BENZENE (THIS CHART)
- BUTADIENE (THIS CHART)
- BUTYLENE (THIS CHART)
- DIISOPROPYL [high anti-knock motor fuel]
- ETHYL ALCOHOL (CHART 8)
- ETHYLBENZENE, styrene (THIS CHART)
- ETHYL ETHER [anesthetic solvent]
- ETHYL HALIDES and POLYHALIDES (CHART 9)
- ETHYL MERCAPTAN (CHART 11)
- ETHYLSULFURIC ACID and DIETHYLSULFATE [ethyl alcohol intermediate]
- ETHYL and ETHYLENE NITRO COMPOUNDS (CHART 10)
- ETHYLENE CHLORHYDRIN [disinfectant insecticide, solvent], dioxane [dye intermediate, solvent], dichlorodiethylether [solvent], ethylene oxide, acrylonitrile [synthetic rubber intermediate], ethylene glycol [antifreeze, dynamite], ethylene glycol derivatives [plastic mediums], acrylic acid, methyl acrylate [plastic intermediate], novocaine [anesthetic]
- ETHYLENE HALIDES (CHART 9)
- ETHYLENE OXIDE, ethylene glycol, ethanolamines, [illegible] cosmetic base
- FORMALDEHYDE (CHART 8)
- INTERMEDIATES for plastics and resins
- MUSTARD GAS [military poison gas]
- NAPHTHALENE (THIS CHART)
- NEOHEXANE [high anti-knock motor fuel]
- OXALIC ACID
- POLYMERS of ETHYLENE [synthetic rubbers and plastics, lubricants and additives], polyethylene
- STYRENE (THIS CHART)
- TOLUENE (THIS CHART)
- VINYL and VINYLIDENE CHLORIDE, textiles and plastics

PROPYLENE

CH_3CHCH_2

Propane, Butane, Heavier Hydrocarbons

FUEL · ANESTHETIC

- ALKYLATE [motor and aviation gasoline]
- ALLYL ALCOHOL, acrolein and allyl derivatives [plastics], allyl ether
- ALLYL CHLORIDE, glycerol, cyclopropane, and ALLYL HALIDES
- AROMATIC and CYCLIC COMPOUNDS
- DIISOBUTYL KETONE and CARBINOL [solvents]
- DIISOPROPYL ETHER [anti-knock compound, solvent]
- HALOGEN DERIVATIVES (CHART 9) propylene glycol
- INTERMEDIATES for plastics and resins
- ISOPHORONE [solvent, chemical intermediate]
- ISOPROPYL ACETATE [solvent]
- ISOPROPYL and n-PROPYL ALCOHOL (CHART 8)
- ISOPROPYL BENZENE (CUMENE) [aviation gasoline]
- ISOPROPYL HALIDES (CHART 9)
- ISOPROPYL and n-PROPYL MERCAPTANS (CHART 11)
- POLYMERS of PROPYLENE [aviation gasoline, lubricants]
- PROPYLENE CHLOROHYDRINS [solvent, dyestuff intermediate], acetone, isopropyl acetate and ether, propylene glycol and derivatives, propylene oxide
- TRIPTANE [high anti-knock motor fuel]

BUTYLENE

$CH_3CHCHCH_3$ or $CH_2CHCH_2CH_3$

Butane, Heavier Hydrocarbons

- ACETYLENE and DERIVATIVES
- ALKYLATES [motor and aviation gasoline]
- AROMATIC and CYCLIC COMPOUNDS
- BUTADIENE (THIS CHART)
- sec BUTYL ALCOHOL (CHART 8)
- BUTYL CHLOROHYDRINS [solvents], butylene glycol and derivatives
- BUTYL MERCAPTANS (CHART 11)
- ETHYLENE and DERIVATIVES
- HALOGEN DERIVATIVES (CHART 9)
- INTERMEDIATES for plastics and resins
- ISOBUTYLENE (THIS CHART)
- METHYL ETHYL KETONE (solvent, dewaxing of oils]
- NITRO COMPOUNDS (CHART 10)
- POLYMERS

ISOBUTYLENE

$(CH_3)_2CHCH_2$

Isobutane, Butane, Heavier Hydrocarbons

- ACETYLENE and DERIVATIVES
- ALKYLATES [motor and aviation gasoline]
- ALKYLATED PHENOLS [antioxidants for petroleum]
- AROMATIC and CYCLIC COMPOUNDS
- BUTADIENE (THIS CHART)
- BUTYLENE (THIS CHART)
- ter-BUTYL ALCOHOL (CHART 8)
- ter-BUTYLPHENOL, resins
- DIISOBUTYLENE, isooctane
- ETHYLENE and DERIVATIVES
- INTERMEDIATES for plastics and resins
- ISOBUTYLENE CHLOROHYDRIN, isobutyric acid and aldehyde, isobutylene glycol
- ISOBUTYLENE HALIDES (CHART 9)
- ISOBUTYL MERCAPTANS (CHART 11)
- METHALLYL ALCOHOL, plastics
- METHALLYL CHLORIDE [fumigant], methyl glycerol
- NITRO COMPOUNDS (CHART 10)
- POLYMERS [lubricant additives, rubber substitutes, butyl rubber]

BUTADIENE

$CH_2CHCHCH_2$

Ethane, Propane, Butane, Heavier Hydrocarbons

- BUTADIENE SULFONES
- HALOGEN DERIVATIVES
- ORGANIC BASES, vulcanization accelerators
- POLYMERIZATION and CONDENSATION PRODUCTS [synthetic rubber, plastics and resins, varnish and varnish oils]

LIQUIDS

BENZENE

C_6H_6

Ethane, Propane, Butane, Heavier Hydrocarbons

SOLVENT · DILUENT · CLEANSING AGENT
MOTOR FUEL

- ALKYL BENZENES, toluene (THIS CHART) styrene
- BENZALDEHYDE [antiseptic, organic synthesis and dyestuff intermediate, perfumes and flavoring extracts, plastics, pharmaceuticals]
- BENZENESULFONIC ACID, benzene derivatives
- CHLOROBENZENES and BENZENE HALIDES [solvents, dyestuff and pharmaceutical intermediates], dichlorodiphenyltrichloroethane [insecticide DDT]
- CHLORONITROBENZENES
- CYCLOHEXANE [solvents, motor fuel]
- MALEIC ACID [rancidity retardant], acrylic acid [plastics], organic chemicals
- MALEIC ANHYDRIDE, alkyd resins
- NITROBENZENE [solvent], aromatic amines
- PHENOL [germicide and disinfectant, organic reagent, solvent, petroleum refining], plastics and resins, adipic acid [intermediate for nylon type plastics]

TOLUENE

$C_6H_5CH_3$

Ethane, Propane, Butane, Heavier Hydrocarbons

SOLVENT · DILUENT · CLEANSING AGENT
MOTOR FUEL

- BENZYL HALIDES, benzaldehyde, dyestuff intermediates
- INTERMEDIATES for dyestuffs and pharmaceuticals
- METHYLCYCLOHEXANE [solvent]
- NITROTOLUENES [high explosives], trinitrotoluene (TNT)
- TOLUENE SULFONIC ACIDS, toluene derivatives, saccharin

OTHER CYCLIC COMPOUNDS -

CYCLOPARAFFINS
CYCLOOLEFINS
INDENES
STYRENE
XYLENE & OTHER ALKYL BENZENES

Natural Gas, Heavier Hydrocarbons

- SOLVENTS · EMULSIFYING AGENTS
- REAGENTS for dyestuff and other organic syntheses
- INTERMEDIATES for synthetic rubber polymers, plastics and resins [Styrene is a copolymer with butadiene for synthetic rubber, also monomer for polystyrene resins]

SOLIDS

NAPHTHALENE

$C_{10}H_8$

Natural Gas

INSECTICIDE

- ADDITIVES for lubricants
- DYESTUFF and PHARMACEUTICAL INTERMEDIATES
- HALOGENATED NAPHTHALENES [oils and waxes]
- NAPHTHALENE SULFONIC ACID, naphthol
- PHTHALIC ACID and ANHYDRIDE esters, alkyd resins
- TETRA- & DECAHYDRONAPHTHALENES [solvents]
- ALKYLATED NAPHTHALENES [fuels]

ANTHRACENE

$C_{14}H_{10}$

Natural Gas

- ALIZARIN DYES
- INTERMEDIATES for dyestuffs and pharmaceuticals

CARBON

C

Natural Gas

- ACTIVATED CARBON
- BRIQUETTES
- CARBON BLACK by (a) channel process, (b) furnace process, (c) thermal decomposition process [ingredient used in rubber compounding and automotive tire manufacturing, pigment in ink and paint, ingredient in insulating compositions, electrodes, enamels and lacquers, hard rubbers and plastics, lubricants, tile and ceramics]
- REAGENT in steel processing

Chart 7 to 11 (General)

In preparing charts 7 to 11, products shown as derivatives of a particular hydrocarbon are not necessarily produced in commercial practice from that hydrocarbon or from a hydrocarbon as the original raw material. They are included, however, as they could be produced as shown if desirable to do so.

Examples of compounds of this type are the "Freons," which are shown as secondary products obtainable from natural-gas hydrocarbons by halogenation. These refrigerants are produced commercially, according to best available information, from carbon tetrachloride or other compounds derived from nonhydrocarbon raw materials. Data on raw materials actually used in commercial production of synthetic chemicals are not revealed by many manufacturers.

Space does not permit naming all possible derivatives or secondary products. For example, one company lists 85 organic chemicals, of which they say: "In producing all these chemicals, olefins derived by processing natural gas are used either directly or indirectly as raw material." Disclosure of scientific information from enemy sources since the recent war show that German technicians produced 37 or more chemical products from acetylene. An American company manufacturing nitration products from natural-gas hydrocarbons lists 54 derivatives as an incomplete list of those that can be made available. A handbook showing uses and applications of chemicals shows butyl alcohol as a reagent in making 132 different compounds. These data show the impracticability of listing all products and indicate the possibilities of chemical production with natural gas as a raw material. The use of heavier petroleum hydrocarbons, which are nongaseous under ordinary conditions, as initial materials for chemical production also should be considered.

Chart 7

The decomposition of natural-gas hydrocarbons into smaller reactive molecules (primary products), which may recombine during the operation to form larger hydrocarbon molecules, either aliphatic or cyclic, or which may be separated and utilized as intermediate products in the production of fuels and chemicals, is perhaps the most important of the processes for conversion of these hydrocarbons. These primary products usually are more susceptible to chemical manipulation than the original molecules.

Thermal (pyrolytic), thermal catalytic, and electrical methods are applied successfully to the decomposition of petroleum and natural-gas hydrocarbons. The first two of these have found greatest application. The electric arc has been reported to have been used successfully for decomposition of natural-gas hydrocarbons; it was used in Germany during the war for the production of acetylene from natural gas or from byproduct gas from coal hydrogenation.

Primary products from natural-gas decomposition shown in chart 7 do not include aliphatic hydrocarbons containing more than four carbon atoms or the less common homologues of acetylene or butadiene that may be formed.

Because of the attention given to some of these primary products in recent years, more individual mention is deserved than can be given in the charts.

Hydrogen is produced from natural gas by thermal decomposition with concurrent production of carbon black. Another process for production of hydrogen from natural gas (by reaction with steam) is shown in the next chart (chart 8) and discussed in the accompanying discussion. Both of these methods are used extensively for the production of hydrogen for use in the hydrogenation of oils, in the manufacture of ammonia, and for other uses.

The production and chemistry of acetylene received much attention long before methods were evolved for its production from natural-gas hydrocarbons. Although acetylene presents some mechanical difficulty in handling because of its tendency to explode under pressure, its use in chemical synthesis has attained a position of importance in American synthetic processes. It is used as the basis for the manufacture of a number of commercial products and was used widely in Germany for production of chemicals needed throughout the war. Ordinarily, acetylene is produced for commercial use from nonhydrocarbon materials, but has been obtained from natural-gas hydrocarbons by thermal decomposition or by use of electric-arc cracking.

Ethylene is an important constituent in refinery gas produced in the manufacture of gasoline from nongaseous petroleum hydrocarbons. It is readily produced by pyrolysis of natural gas. Propylene, butylene, and iso-butylene are produced similarly. These unsaturated hydrocarbons are of the type known as olefins and form the basis for the manufacture of a broad series of organic chemicals. Ethylene, which has been termed a "building block" for organic synthesis, is the starting point for the commercial production of more than 50 products. A correspondingly large number of products is obtained from propylene, butylene, and isobutylene. In the manufacture of aviation fuels and alkylates, these olefins are of prime importance. The production of butadiene has been discussed previously (chart 5).

Besides heavier aliphatic hydrocarbons, not included separately in the chart, that may be formed as the result of decomposition of natural-gas hydrocarbons, a group of cyclic compounds may be formed, which include benzene, toluene, xylene, and other aromatic compounds. However, selected cuts of heavier hydrocarbons from petroleum used as feed stock in catalytic aromatization gives high yields of benzene or toluene, and much of the toluene needed for wartime demands was obtained by this method.

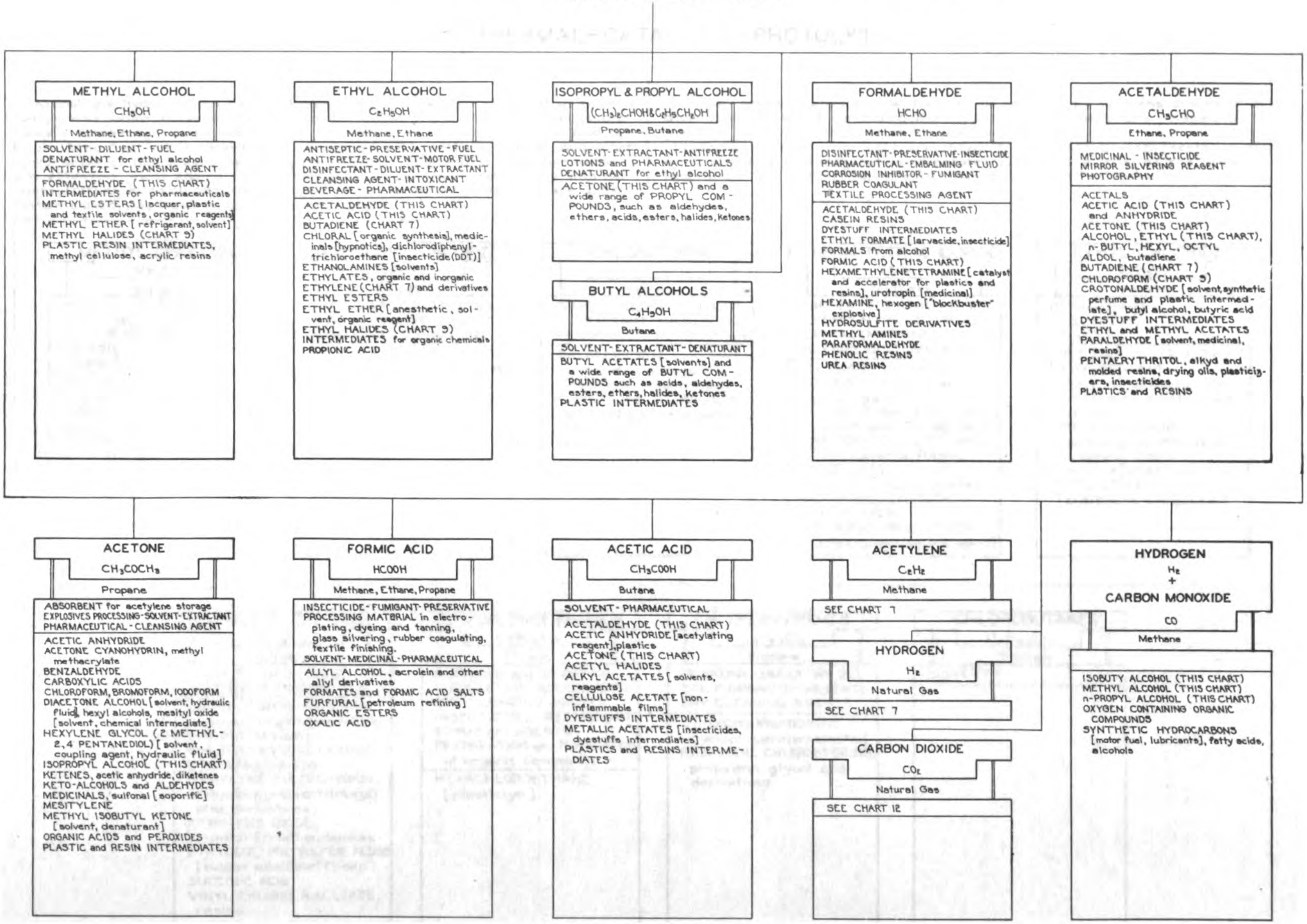
The use of natural gas for the production of carbon black was one of its first non-energy uses. Three methods, known as the channel, thermal decomposition, and furnace processes, are used for the production of carbon black. Each process yields a product of different type especially suited for specific uses. Carbon black is an essential ingredient in the manufacture of automobile tires and other rubber goods and in the production of paints, inks, and other materials. A type of carbon black known as "acetylene black" is produced by the electrical decomposition of acetylene.

Original from THE OHIO STATE UNIVERSITY

CHART 8

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY OXIDATION

THERMAL - CATALYTIC - PRESSURE



METHYL ALCOHOL
CH_3OH
Methane, Ethane, Propane

SOLVENT - DILUENT - FUEL
DENATURANT for ethyl alcohol
ANTIFREEZE - CLEANSING AGENT

FORMALDEHYDE (THIS CHART)
INTERMEDIATES for pharmaceuticals
METHYL ESTERS [lacquer, plastic and textile solvents, organic reagents]
METHYL ETHER [refrigerant, solvent]
METHYL HALIDES (CHART 9)
PLASTIC RESIN INTERMEDIATES, methyl cellulose, acrylic resins

ETHYL ALCOHOL
C_2H_5OH
Methane, Ethane

ANTISEPTIC - PRESERVATIVE - FUEL
ANTIFREEZE - SOLVENT - MOTOR FUEL
DISINFECTANT - DILUENT - EXTRACTANT
CLEANSING AGENT - INTOXICANT
BEVERAGE - PHARMACEUTICAL

ACETALDEHYDE (THIS CHART)
ACETIC ACID (THIS CHART)
BUTADIENE (CHART 7)
CHLORAL [organic synthesis], medicinals [hypnotics], dichlorodiphenyl-trichloroethane [insecticide (DDT)]
ETHANOLAMINES [solvents]
ETHYLATES, organic and inorganic
ETHYLENE (CHART 7) and derivatives
ETHYL ESTERS
ETHYL ETHER [anesthetic, solvent, organic reagent]
ETHYL HALIDES (CHART 9)
INTERMEDIATES for organic chemicals
PROPIONIC ACID

ISOPROPYL & PROPYL ALCOHOL
$(CH_3)_2CHOH$ & $C_2H_5CH_2OH$
Propane, Butane

SOLVENT - EXTRACTANT - ANTIFREEZE
LOTIONS and PHARMACEUTICALS
DENATURANT for ethyl alcohol

ACETONE (THIS CHART) and a wide range of PROPYL COMPOUNDS, such as aldehydes, ethers, acids, esters, halides, Ketones

BUTYL ALCOHOLS
C_4H_9OH
Butane

SOLVENT - EXTRACTANT - DENATURANT

BUTYL ACETATES [solvents] and a wide range of BUTYL COMPOUNDS such as acids, aldehydes, esters, ethers, halides, ketones
PLASTIC INTERMEDIATES

FORMALDEHYDE
HCHO
Methane, Ethane

DISINFECTANT - PRESERVATIVE - INSECTICIDE
PHARMACEUTICAL - EMBALMING FLUID
CORROSION INHIBITOR - FUMIGANT
RUBBER COAGULANT
TEXTILE PROCESSING AGENT

ACETALDEHYDE (THIS CHART)
CASEIN RESINS
DYESTUFF INTERMEDIATES
ETHYL FORMATE [larvacide, insecticide]
FORMALS from alcohol
FORMIC ACID (THIS CHART)
HEXAMETHYLENETETRAMINE [catalyst and accelerator for plastics and resins], urotropin [medicinal]
HEXAMINE, hexogen ["blockbuster" explosive]
HYDROSULFITE DERIVATIVES
METHYL AMINES
PARAFORMALDEHYDE
PHENOLIC RESINS
UREA RESINS

ACETALDEHYDE
CH_3CHO
Ethane, Propane

MEDICINAL - INSECTICIDE
MIRROR SILVERING REAGENT
PHOTOGRAPHY

ACETALS
ACETIC ACID (THIS CHART) and ANHYDRIDE
ACETONE (THIS CHART)
ALCOHOL, ETHYL (THIS CHART), n-BUTYL, HEXYL, OCTYL
ALDOL, butadiene
BUTADIENE (CHART 7)
CHLOROFORM (CHART 9)
CROTONALDEHYDE [solvent, synthetic perfume and plastic intermediate], butyl alcohol, butyric acid
DYESTUFF INTERMEDIATES
ETHYL and METHYL ACETATES
PARALDEHYDE [solvent, medicinal, resins]
PENTAERYTHRITOL, alkyd and molded resins, drying oils, plasticizers, insecticides
PLASTICS and RESINS

ACETONE
CH_3COCH_3
Propane

ABSORBENT for acetylene storage
EXPLOSIVES PROCESSING - SOLVENT - EXTRACTANT
PHARMACEUTICAL - CLEANSING AGENT

ACETIC ANHYDRIDE
ACETONE CYANOHYDRIN, methyl methacrylate
BENZALDEHYDE
CARBOXYLIC ACIDS
CHLOROFORM, BROMOFORM, IODOFORM
DIACETONE ALCOHOL [solvent, hydraulic fluid], hexyl alcohols, mesityl oxide [solvent, chemical intermediate]
HEXYLENE GLYCOL (2 METHYL-2,4 PENTANEDIOL) [solvent, coupling agent, hydraulic fluid]
ISOPROPYL ALCOHOL (THIS CHART)
KETENES, acetic anhydride, diketenes
KETO-ALCOHOLS and ALDEHYDES
MEDICINALS, sulfonal [soporific]
MESITYLENE
METHYL ISOBUTYL KETONE [solvent, denaturant]
ORGANIC ACIDS and PEROXIDES
PLASTIC and RESIN INTERMEDIATES

FORMIC ACID
HCOOH
Methane, Ethane, Propane

INSECTICIDE - FUMIGANT - PRESERVATIVE
PROCESSING MATERIAL in electroplating, dyeing and tanning, glass silvering, rubber coagulating, textile finishing.
SOLVENT - MEDICINAL - PHARMACEUTICAL

ALLYL ALCOHOL, acrolein and other allyl derivatives
FORMATES and FORMIC ACID SALTS
FURFURAL [petroleum refining]
ORGANIC ESTERS
OXALIC ACID

ACETIC ACID
CH_3COOH
Butane

SOLVENT - PHARMACEUTICAL

ACETALDEHYDE (THIS CHART)
ACETIC ANHYDRIDE [acetylating reagent], plastics
ACETONE (THIS CHART)
ACETYL HALIDES
ALKYL ACETATES [solvents, reagents]
CELLULOSE ACETATE [non-inflammable films]
DYESTUFFS INTERMEDIATES
METALLIC ACETATES [insecticides, dyestuffs intermediates]
PLASTICS and RESINS INTERMEDIATES

ACETYLENE
C_2H_2
Methane

SEE CHART 7

HYDROGEN
H_2
Natural Gas

SEE CHART 7

CARBON DIOXIDE
CO_2
Natural Gas

SEE CHART 12

HYDROGEN
H_2
+
CARBON MONOXIDE
CO
Methane

ISOBUTY ALCOHOL (THIS CHART)
METHYL ALCOHOL (THIS CHART)
n-PROPYL ALCOHOL (THIS CHART)
OXYGEN CONTAINING ORGANIC COMPOUNDS
SYNTHETIC HYDROCARBONS [motor fuel, lubricants], fatty acids, alcohols

CHART 9

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY HALOGENATION

THERMAL-CATALYTIC-PHOTOLYTIC

Natural gas hydrocarbons can undergo direct fluorination, chlorination, bromination, and iodination when reacted under proper conditions with halogens or halogen-containing compounds. Direct fluorination is said to be violent and difficult to control but is reported accomplished with methane, ethane, and other hydrocarbons. Iodination is a reversible reaction. Bromination and chlorination are effected most easily. Olefin hydrocarbons generally react easily with halogens, forming addition compounds; substitutive halogenation takes place under certain conditions, forming allylic halides (Chart 7).

Halogen atoms in aliphatic halides may be replaced by halogens preceding in the atomic series. Fluoro- or fluorochlorohydrocarbons usually are obtained by replacement of chlorine with fluorine in chlorohydrocarbons.

Products of chlorination only are shown in this chart as representative of products obtained by halogenation of natural gas hydrocarbons, as the greatest laboratory and commercial attention has been given to chlorination.

METHYL CHLORIDE
CH_3Cl
Methane

SOLVENT-EXTRACTANT
ANESTHETIC-REFRIGERANT
CLEANSING AGENT
CHLORINATING & METHYLATING AGENT

ACETYL CHLORIDE [organic reagent], dyestuffs
FORMALDEHYDE (CHART 8)
METHYL ALCOHOL (CHART 8)
METHYLENE CHLORIDE

METHYLENE CHLORIDE
CH_2Cl_2
Methane

ANESTHETIC-EXTRACTANT
CLEANSING AGENT-SOLVENT
INSECTICIDE-REFRIGERANT

ACETIC ANHYDRIDE
CHLOROACETALDEHYDE [solvent]
FORMALDEHYDE
INTERMEDIATES for organic chemicals, pharmaceuticals

CHLOROFORM
$CHCl_3$
Methane

SOLVENT-CLEANSING AGENT
EXTRACTANT-ANESTHETIC
PHARMACEUTICAL-PRESERVATIVE

CHLOROPICRIN, carbonyl chloride (phosgene) [military poison gas]
FLUORO- and FLUOROCHLOROMETHANES [refrigerants (freons)]
MEDICINALS

CARBON TETRACHLORIDE
CCl_4
Methane

FIRE EXTINGUISHER FLUID
CLEANSING AGENT-SOLVENT
EXTRACTANT-INSECTICIDE
REFRIGERANT-MEDICINAL

CARBONYL CHLORINE (PHOSGENE) [military poison gas]
CHLOROFORM (THIS CHART)
FLUORO- and FLUOROCHLOROMETHANES and ETHANES [refrigerants (freons)]
HEXACHLOROETHANE [solvent, organic synthesis]
METHYLENE CHLORIDE (THIS CHART)
TETRACHLOROETHYLENE [solvent, dry cleaning agent]

ETHYL CHLORIDE
C_2H_5Cl
Ethane

REFRIGERANT
ANESTHETIC
SOLVENT

DYESTUFF INTERMEDIATES
ETHYLBENZENE, styrene [synthetic rubber copolymer], plastics and resins
ETHYL CELLULOSE [plasticizer], transparent wrapping films
ETHYL MERCAPTAN (CHART 11)
TETRAETHYLLEAD [antiknock compound]

ETHYLENE CHLORIDE
$C_2H_4Cl_2$
Ethane

SOLVENT-ANESTHETIC
ANTI-KNOCK FLUID ADDITIVE

β,β′ DICHLOROETHYL ETHER [solvent in petroleum refining]
DIOXANE [solvent]
DI-& TRIETHYLENE GLYCOLS
ETHYLENEDIAMINE
ETHYLENE CHLOROHYDRIN, ethylene glycol [antifreeze] and derivatives
ETHYLENE OXIDE, mono-di-& triethanolamines
ETHYLENE POLYSULFIDE RESINS [rubber substitute (Thiokol)]
SUCCINIC ACID
VINYL CHLORIDE & ACETATE, resins

POLYCHLOROETHANES
$C_2H_{6-x}Cl_x$
Ethane

REFINING and DEWAXING
LUBRICATING OILS-SOLVENTS
DRY CLEANING AGENTS
INSECTICIDES-REFRIGERANTS
FLOTATION AGENTS
PREPARATION and PURIFICATION of organic compounds

HEXACHLOROETHANE [plasticizer]

CHLOROPROPANES
$C_3H_{8-x}Cl_x$
Propane

DEWAXING LUBRICATING OILS
SOIL FUMIGANTS-SOLVENTS
DRY CLEANING AGENTS

1, 3-DICHLOROPROPANE cyclopropane [anesthetic]
PROPYLENE CHLOROHYDRINS, propylene glycol and derivatives

CHLOROBUTANES
$C_4H_{10-x}Cl_x$
Butanes

SOLVENTS

Chart 8

Oxidation of the hydrocarbons in natural gas in the form of combustion furnishes the basis for its use as a heat and energy source. The ultimate products of combustion of hydrocarbons are carbon dioxide and water. Controlled and limited oxidation of hydrocarbons produces a number of products highly useful in the production of textiles and plastics and in other industries. Among the oxidation products obtainable from natural gas and other petroleum hydrocarbons are alcohols, acids, fatty acids, and aldehydes. Those of most importance produced commercially from natural gas include methyl, ethyl, isopropyl, propyl, and butyl alcohols, formaldehyde and acetaldehyde, acetone, methylacetone, acetic acid, acetic anhydride, propionic acid, and many derivatives. Both saturated and unsaturated aliphatic hydrocarbons are utilized, ordinarily in the presence of a catalyst, in the production of oxidation products.

The reaction of natural-gas hydrocarbons with steam, oxygen, and carbon dioxide to form a "synthesis gas" for the Fischer-Tropsch synthesis of higher hydrocarbons has reveived much recent attention as a possible method for utilization of methane in the manufacture of motor fuels. In addition, organic chemicals such as alcohols, aldehydes, acids, and esters can be produced concurrently with the motor fuel.

The reaction of methane and steam when carried to completion gives carbon dioxide and hydrogen. This reaction has been the basis for production of hydrogen for many of the plants that produced ammonia and nitric acid for wartime use. Natural gas or hydrogen from natural gas also is used in the manufacture of pure nitrogen from air for use in ammonia manufacture. By means of controlled combustion, the oxygen content of air is removed, leaving nitrogen, carbon dioxide, and water, which are easily separated. Possible byproducts and derivatives besides ammonium nitrate in the manufacture of ammonia and nitric acid include methyl alcohol from hydrogen and carbon monoxide, formaldehyde from methyl alcohol, dry ice from waste carbon dioxide, urea from liquid ammonia and carbon dioxide, and perhaps ammonium sulfate, sodium carbonate, sodium nitrate, dicalcium phosphate, hydrogen cyanide, formamide, and others.

Chart 9

Chart 9 shows products of chlorination as representatives of products obtainable by halogenation of natural gas. Chlorinated hydrocarbons form an important class of chemicals, which are used directly as solvents, refrigerants, degreasing compounds, and for many other purposes; also as intermediates in organic chemical synthesis. Fluoro and fluorochloro compounds, which are used principally as refrigerants, usually are obtained by replacement of chlorine with fluorine in a chloro compound. A few brominated hydrocarbons are in commercial production. Methyl bromide is used as a fumigant and insecticide. Ethylene dibromide is used in tetraethyllead fluids, as a solvent, and as an intermediate in the production of a number of chemicals.

Chart 10

Active research into the nitration of natural-gas hydrocarbons began around 1930 and has produced a variety of products. Commercial production of nitroparaffins by use of the vapor-phase nitration reaction of nitric acid and hydrocarbons from petroleum and natural gas, occurred within the present decade. Uses for these nitroparaffins and their derivatives in many fields already have been developed, and other extensive uses have been prophesied.

Chart 11

Chart 11 shows products obtainable from natural gas and other petroleum hydrocarbons by sulfurization. Production of these products is small, but recent announcements indicate future commercial-scale manufacture of carbon disulfide, thiophene, mercaptans, thioethers, and other sulfur compounds, using natural gas and sulfur or hydrogen sulfide as starting materials. Butyl mercaptan and butyl disulfide are said to be available already in tank-car lots, and other sulfur compounds are being produced in experimental or pilot-plant quantities. One company states that a plant was erected and operated successfully for the manufacture of tertiary dodecyl mercaptan (C_{12}), using as raw materials hydrogen sulfide derived from natural gas, with copolymers from propylene and isobutylene resulting from thermal decomposition of isobutane. The plant was built in anticipation of a demand for the product in the synthetic-rubber program but was shut down when the demand did not materialize. Another company has announced the pilot plant and contemplated commercial production of thiophene. Still another company has announced the pilot-plant development of a process for the manufacture of carbon disulfide by the catalytic reaction of sulfur and hydrocarbons from natural gas.

Many of the uses for sulfurization products shown in chart 11 are those suggested by manufacturers as possible uses and have not yet been been proven commercially.

Chart 12

Nonhydrocarbon constituents of natural gas usually are present in relatively small amounts. Some of these materials, such as helium, are of enough value to warrant their recovery even when present in quantities of only a few percent. Others, such as hydrogen sulfide, usually are objectionable and ordinarily must be removed before the hydrocarbon content of the gas can be utilized. Hydrogen sulfide and other objectionable gases may become valuable when separated and used in the production of other products. The use of hydrogen sulfide in the production of sulfur compounds from hydrocarbons already has been mentioned. In at least one natural-gas field it is recovered and used for the production of elemental sulfur.

Some natural gases are composed almost entirely of carbon dioxide. Carbon dioxide from this source may be of value if the wells from which it is produced are geographically situated where the gas may be utilized economically. So far, no economic use for nitrogen in natural gas has been developed.

CHART 10

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY NITRATION

THERMAL

NITROMETHANE
CH_3NO_2
Methane, Propane, Butane

NITROETHANE
$C_2H_5NO_2$
Ethane

NITROPROPANES
$C_3H_7NO_2$
Propane, Isobutane

NITROBUTANES
$C_4H_9NO_2$
Butane, Isobutane

SOLVENTS - PAINT and VARNISH REMOVERS
HEAT SENSITIZERS for rubber latex

ALDEHYDES and KETONES
ALDOXIMES
ALKYLHYDROXYLAMINES
AMINES and DIAMINES, synthetic drugs, organic intermediates
AMINOHYDROXYL COMPOUNDS: AMINOALCOHOLS, AMINOGLYCOLS, AMINOALKENETRIOLS and AMINOACETALS, soaps of preceding compounds [emulsifying agents, cosmetics]
CARBOXYLIC ACIDS
CHLORONITRO PARAFFINS and CHLORONITRO ALCOHOLS, 1,1-dichloronitroethane [insecticide (Ethide)], chloropicrin [lachrymator, fumigant, and soil-sterilizing agent]
DINITROPARAFFINS
HYDROXAMIC ACIDS
HYDROXYLAMINE [organic reducing agent] and HYDROXYLAMINE SALTS, hydroxylamine acid sulfate, oximes, hydroxylamine sulfate [intermediates for dyestuffs, pharmaceuticals, resins, flotation agents]
KETOXIMES
NITROAMINES, diamines
NITROHYDROXYL COMPOUNDS: NITROALCOHOLS, NITROGLYCOLS, NITROALKANETRIOLS, organic and inorganic esters of preceding compounds [explosives intermediates], aminohydroxyl compounds
NITROKETONES
NITROOLEFINS

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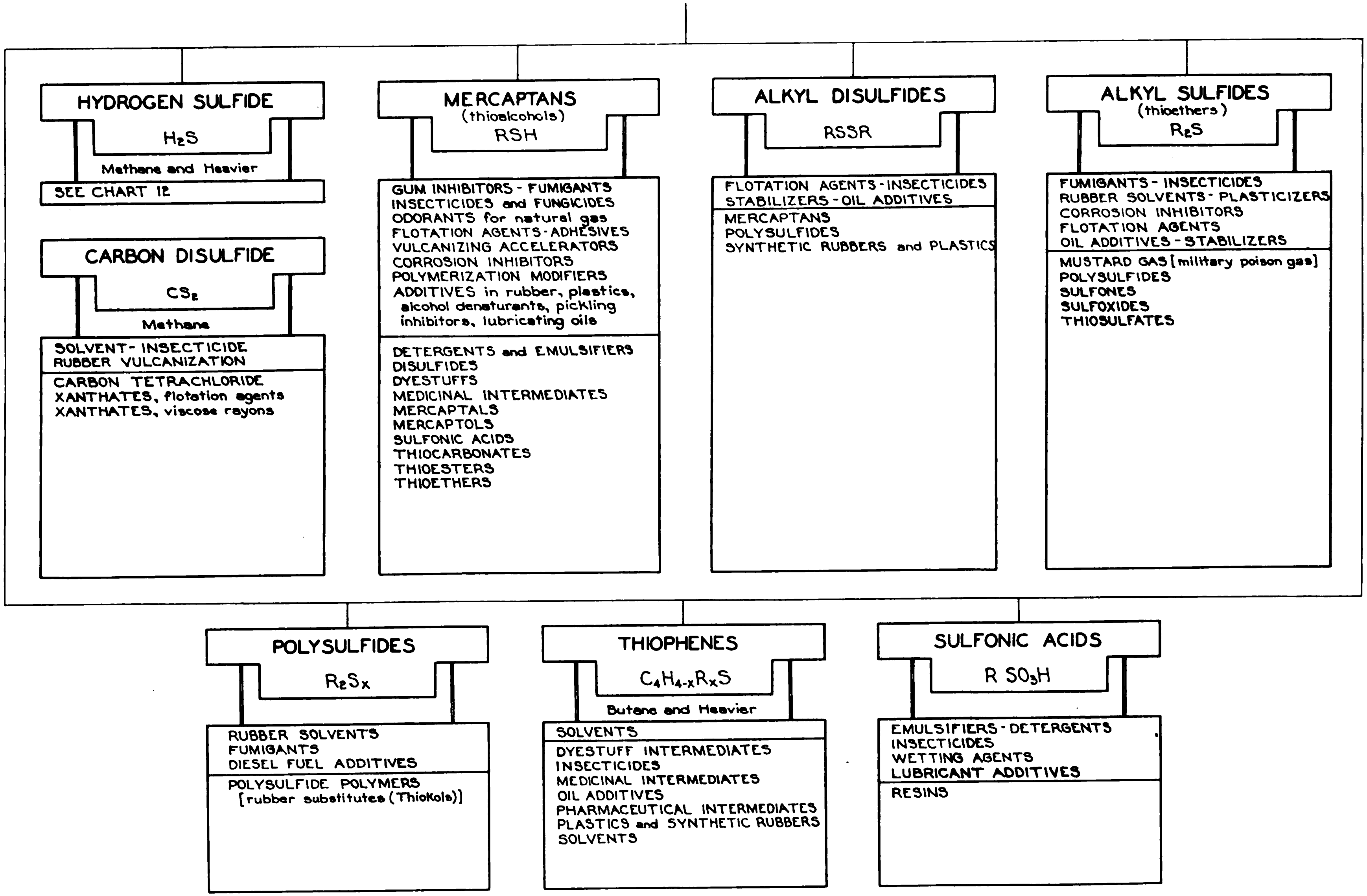
CHART II

PRODUCTS OBTAINABLE FROM NATURAL GAS AND OTHER PETROLEUM HYDROCARBONS BY SULFURIZATION



HYDROGEN SULFIDE
H_2S
Methane and Heavier
- SEE CHART 12

CARBON DISULFIDE
CS_2
Methane
- SOLVENT - INSECTICIDE
- RUBBER VULCANIZATION

- CARBON TETRACHLORIDE
- XANTHATES, flotation agents
- XANTHATES, viscose rayons

MERCAPTANS
(thioalcohols)
RSH
- GUM INHIBITORS - FUMIGANTS
- INSECTICIDES and FUNGICIDES
- ODORANTS for natural gas
- FLOTATION AGENTS - ADHESIVES
- VULCANIZING ACCELERATORS
- CORROSION INHIBITORS
- POLYMERIZATION MODIFIERS
- ADDITIVES in rubber, plastics, alcohol denaturants, pickling inhibitors, lubricating oils

- DETERGENTS and EMULSIFIERS
- DISULFIDES
- DYESTUFFS
- MEDICINAL INTERMEDIATES
- MERCAPTALS
- MERCAPTOLS
- SULFONIC ACIDS
- THIOCARBONATES
- THIOESTERS
- THIOETHERS

ALKYL DISULFIDES
RSSR
- FLOTATION AGENTS - INSECTICIDES
- STABILIZERS - OIL ADDITIVES

- MERCAPTANS
- POLYSULFIDES
- SYNTHETIC RUBBERS and PLASTICS

ALKYL SULFIDES
(thioethers)
R_2S
- FUMIGANTS - INSECTICIDES
- RUBBER SOLVENTS - PLASTICIZERS
- CORROSION INHIBITORS
- FLOTATION AGENTS
- OIL ADDITIVES - STABILIZERS

- MUSTARD GAS [military poison gas]
- POLYSULFIDES
- SULFONES
- SULFOXIDES
- THIOSULFATES

POLYSULFIDES
R_2S_x
- RUBBER SOLVENTS
- FUMIGANTS
- DIESEL FUEL ADDITIVES

- POLYSULFIDE POLYMERS [rubber substitutes (Thiokols)]

THIOPHENES
$C_4H_{4-x}R_xS$
Butene and Heavier
- SOLVENTS

- DYESTUFF INTERMEDIATES
- INSECTICIDES
- MEDICINAL INTERMEDIATES
- OIL ADDITIVES
- PHARMACEUTICAL INTERMEDIATES
- PLASTICS and SYNTHETIC RUBBERS
- SOLVENTS

SULFONIC ACIDS
$R\ SO_3H$
- EMULSIFIERS - DETERGENTS
- INSECTICIDES
- WETTING AGENTS
- LUBRICANT ADDITIVES

- RESINS

CHART 12

USES OF NON-HYDROCARBON NATURAL GAS CONSTITUENTS

HELIUM

He

- OXYGEN DILUENT for diving and caisson work and medicinal purposes
- PRESERVATIVE
- INFLATION of lighter-than-air ships, toy and meteorological balloons
- PROCESSING of special steels
- ELECTRIC DISCHARGE TYPE SIGNS
- TRACER GAS to determine direction of flow in petroleum reservoirs
- SHIELD to prevent oxidation in magnesium and stainless steel welding
- DILUENT to reduce explosiveness in anesthesia

HYDROGEN SULFIDE

H_2S

- LABORATORY REAGENT in analytical procedure

- CARBON DISULFIDE
- HYDROGEN CHLORIDE
- MERCAPTANS
- SULFUR
- SULFUR DIOXIDE, sulfuric acid
- THIOETHERS
- THIOSULFATES

CARBON DIOXIDE

CO_2

- REFRIGERANT (DRY ICE)
- FIRE EXTINGUISHER
- FOOD PRESERVATIVE
- BEVERAGE CARBONATOR

- AMMONIUM CARBAMATE, urea
- CARBON MONOXIDE and HYDROGEN (CHART 8)
- CARBONATES, INORGANIC
- VARIOUS ORGANIC CHEMICALS

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SELECTED REFERENCES

General

1. Oil and Gas Jour., Blueprint of Refinery Processes: Vol. 43, Mar. 31, 1945, pp. 169-216.
2. Fortune, Carbide and Carbon Chemicals Juggle the Molecules of Natural, Coke-Oven, and Petroleum Gases into a $62,000,000 Starburst of New Materials: Vol. 24, Sept. 1941, pp. 56-67+.
3. Chem. and Met. Eng., Petroleum Byproducts a Big Factor in Organic Chemical Industry: Vol. 52, Dec. 1945, pp. 121-128.
4. Ind. Eng. Chem., Symposium on Utilization of Gaseous Hydrocarbons: Vol. 24, Jan. 1932, pp. 10-27.
5. Ind. Eng. Chem., Symposium on Synthetic Rubber and Elastic Polymers: Vol. 31, Aug. 1939, pp. 934-968.
6. Armistead, George, Jr., Chemical Conversions of Lighter Hydrocarbons: Ref. and Nat. Gaso. Mfg., vol. 20, Sept. 1941, pp. 67-76.
7. Bludworth, J. E., Chemicals from Lighter Hydrocarbons: Petrol. Refiner, vol. 25, May 1946, pp. 102-105.
8. Brooks, B. T., Synthetic Organic Chemicals from Petroleum - An American Development: Ind. Eng. Chem., vol. 31, May 1939, pp. 515-519.

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9. Cooke, M. B., Wagner, C. R., and Swanson, H. R., Organic Chemicals from Petroleum and Natural Gas: Proc. Second World Petrol. Cong., Paris, 1937, vol. 2, pp. 477-488.

10. Egloff, Gustav, Synthetic Products from Petroleum: Jour. Inst. Petrol. Tech., vol. 23, 1937, pp. 645-668.

11. Egloff, Gustav, Present and Future Products and Chemicals made from Natural Gases, vol. 1, Oct. 1945, pp. 7-10.

12. Egloff, Gustav, The Reactions of Pure Hydrocarbons: Reinhold Pub. Corp., New York, 1937, 897 pp.

13. Egloff, Gustav, and Wilson, Edith, Thermal Reactions of Gaseous Hydrocarbons: Ind. Eng. Chem., vol. 27, Aug. 1935, pp. 917-933.

14. Egloff, Gustav, Wilson, Edith, Hulla, George, and Van Arsdell, P. M., The Reactions of Pure Hydrocarbons in the Presence of Aluminum Chloride: Chem. Rev., vol. 20, June 1937, pp. 346-411.

15. Ellis, Carleton, The Chemistry of Petroleum Derivatives: Reinhold Pub. Co., New York, vol. 1, 1934, 1285 pp.; vol. 2, 1937, 1464 pp.

16. Foster, A. L., Chemical Utilization of Natural Gas; Oil and Gas Jour., vol. 45, May 4, 1946, pp. 83-84, 91.

17. Frolich, P. K., Chemical Trends in the Petroleum Industry: Ind. Eng. Chem., vol. 30, Aug. 1938, pp. 916-922.

18. Heineman, Heinz, Digest of United States Patents on the Recovery and Processing of Natural Gas and on Hydrocarbon Synthesis: Petrol. Refiner, vol. 23, July 1944, pp. 172, 174, 178, 180, 182, 184.

19. Hohenadel, Harry P., Products from Synthesis of Petroleum and Natural Gas: Oil Weekly, vol. 120, Feb. 18, 1946, pp. 27-28; Mining and Metallurgy, vol. 26, Nov. 1945, pp. 576-578.

20. Holliman, W. C., Synthetic Rubber; Its Production from Petroleum, Coal and Other Materials: Bureau of Mines Information Circular 7242, May 1943, 36 pp.

21. Ipatieff, V. N., Catalytic Reactions at High Pressure and Temperatures: Macmillan Co., New York, 1936, 786 pp.

22. McClure, H. B., Industrial Applications of the Glycols: Ind. Eng. Chem., news ed., vol. 17, Mar. 10, 1939, pp. 149-153.

23. Oberfell, G. G., Utilization of Natural Gas in the United States: Gas Age, Dec. 27, 1945, pp. 12-15, 50; Jan. 10, 1946, pp. 25-29, 58; Petrol. Refiner, Jan. 1946, pp. 94-104; (cond.) Oil and Gas Jour., vol. 44, Dec. 15, 1945, pp. 76-78; Amer. Gas Assn. Mo., vol. 28, Jan. 1946, pp. 7-13 48; Mining and Metallurgy, vol. 27, No. 471, Mar. 1946, pp. 165-172.

24. Pew, James E., and Dotterweich, Frank H., Science in Natural Gas: Nat. Petrol. News, vol. 37, Jan. 3, 1945, pp. R11-14; Petrol. Refiner, vol. 23, Dec. 1944, pp. 92-96; Gas Age, vol. 94, Dec. 14, 1944, pp. 19-21+; Amer. Gas Assn. Mo., vol. 27, Mar. 1945, pp. 103-106.

25. McAllister, S. H., High Antiknock Aviation Fuels from Light Hydrocarbons Oil and Gas Jour., vol. 39, Nov. 28, 1940, pp. 42, 45, 47-48.

26. Miller, Benjamin, Chemical Utilization of Natural Gas: Petrol. Refiner, vol. 24, May 1945, pp. 121-124; Petrol. Eng., vol. 16, May 1945, pp. 216-228; Oil Weekly, vol. 117, Apr. 30, 1945, pp. 50-54; Nat. Petrol. News, vol. 37, June 6, 1945, pp. R430-436; (abs.) Chem. Ind., vol. 56, May 1945, pp. 786-788; (cond.) Amer. Gas Jour., vol. 163, July 1945, pp. 36-39; (abs.) Can. Chem. and Process Ind., vol. 29, June 1945, pp. 424+.

27. Raigorodsky, P. M., and Dotterwiech, F. H., War Products from Natural Gas and Natural Gasoline: Oil and Gas Jour., vol. 41, Apr. 15, 1943, pp. 94, 97, 98, 102, 104, and 107; Gas Age, vol. 92, July 29, 1943, pp. 19-23; Petrol. Eng., vol. 14, July 1, 1943 (ref. annual), pp. 198-200, 202-203; Petrol. Refiner, vol. 23, May 1943, pp. 83-89; (abs.) Nat. Petrol. News, vol. 35, April 14, 1943, pp. 14-16.

28. Rosenstein, L., Synthetic Chemicals from Petroleum: A.P.I. Proceedings, vol. 21, sec. III, Nov. 1940, pp. 37-42.

29. Sachanen, A. N., Conversion of Petroleum; Production of Motor Fuels by Thermal and Catalytic Processes: Reinhold Pub. Corp., New York, 1940, 413 pp.

30. Segeler, C. G., Chemical Uses of Gas: Ind. Eng. Chem., news ed., vol. 18, May 25, 1940, pp. 437-438.

31. Smith, Sir Frank, Synthetic Chemicals from Petroleum: Petrol., vol. 8, Sept. 1945, p. 163+; Oct. 1945, p. 184+; Nov. 1945, p. 206+.

32. Steacie, E. W. R., The Kinetics of Elementary Reactions of the Simple Hydrocarbons: Chem. Rev., vol. 22, Apr. 1938, pp. 311-402.

33. Storch, H. H., Physical Chemical Properties of Methane: Bureau of Mines Inf. Circ. 6549, 1932, 14 pp.

34. Thornton, D. P., Jr., Petrochemical Industry in the Southwest Builds for Peacetime Markets: Nat. Petrol. News, vol. 38, Jan. 2, 1946, pp. R3-8.

35. U. S. Tariff Commission, Synthetic Resins and Their Raw Materials: Rep. 131, 2d ser., 1938.

36. Wakeman, R. L., Plastics and the Gas Industry: Amer. Gas. Assn. Proc., 1940, pp. 751-760.

37. Wakeman, R. L., and Weil, B. H., ABC of Chemical Derivatives from Petroleum:
    1. Synthetic Resins and Plastics; Nat. Petrol. News, vol. 34, Nov. 25, 1942, pp. R412-416, R418.
    2. Synthetic Rubbers; Ibid., vol. 35, Jan. 6, 1943, pp. 823-31.
    3. Textile Fibers and Finishing Agents: Ibid., Feb. 3, 1943, pp. R60-65.
    4. Solvents and Plasticizers: Ibid., Mar. 3, 1943, pp. R107-112.
    5. Detergents and Lubricants; Ibid., Apr. 7, 1943, pp. R161-167.
    6. Aviation Gasoline nad Basic Hydrocarbon Fractions: Ibid., May 5, 1943, pp. R213-215, R220-221.
    7. Basic Economics of Petroleum Chemicals Field: Ibid., June 2, 1943, pp. R264-270.

38. Weil, B. H., Plastics from Petroleum: Petrol. Refiner, vol. 24, Jan. 1945, pp. 89-98.

39. Weil, B. H., Synthetics from Petroleum: Petrol. Eng., vol. 16, May 1945, pp. 198-208.

40. Whitmore, F. C., Organic Chemistry: D. van Nostrand Co., New York, 1937, 1080 pp.

41. Williams, E. C., Modern Petroleum Research: Ind. Eng. Chem., news ed., vol. 16, Dec. 10, 1938, pp. 630-632.

42. Williams, E. C., Creating Industries; 1919-1939 - Petroleum: Chem. Ind., vol. 44, May 1939, p. 495.

43. Wilson, R. E., Refinery Gas; A Raw Material of Growing Importance: Chem. and Ind., vol. 58, Dec. 23, 1939, pp. 1095-1101; (cond.) Nat. Petrol. News, vol. 31, Dec. 13, 1939, pp. R541-542+; (abs.) Ind. Eng. Chem., news ed., vol. 17, Nov. 20, 1939, pp. 697-698.

Decomposition

44. Nat. Petrol. News, Acetylene Production by Electric Arc Cracking, and Its Purification: Vol. 37, Nov. 7, 1945, pp. R866, R868.
45. Nat. Petrol. News, Acetylene and Other War Chemicals Made by Cracking in a Regererative Furnace: Vol. 34, Aug. 26, 1942, pp. R270-272, R274-276.
46. Chem. and Met. Eng., Wartime Chemical Developments in German Industry; Acetylene Production and Utilization: Vol. 52, Sept. 1945, pp. 188+.
47. Arnold, P. M., Olefin Production by Thermal Cracking of Isobutane: Oil and Gas Jour., vol. 44, July 7, 1945, pp. 87-88, 92, 95-96, 99.
48. Cohan, Leonard, H., Carbon Black in War and Peace: Chem. and Eng. News, vol. 23, Nov. 25, 1945, pp. 2078-2085, 2145.
49. Dotterweich, Frank H., Natural Gas as a Raw Material in the Production of Synthetic Ammonia: Refiner and Nat. Gaso. Mfg., vol. 21, Mar. 1942, pp. 51-55.
50. Dunstan, A. E., Hague, E. N., and Wheeler, R. V. Thermal Treatment of Gaseous Hydrocarbons. 1. Laboratory Scale Operation: Ind. Eng. Chem., vol. 26, Mar. 1934, pp. 307-314.
51. Edgar, Graham, Tetraethyllead, Manufacture and Use: Ind. Eng. Chem., vol. 31, Dec. 1939, pp. 1439-1446.
52. Egloff, G., and Hulla, G., Conversion of Hydrocarbons into Butadiene: Chem. Rev., vol. 35, Oct. 1944, pp. 279-333.
53. Egloff, G., Schaad, R. E., and Lowry, C. D., Jr., The Decomposition of the Paraffin Hydrocarbons: Jour. Phys. Chem., vol. 34, 1930, pp. 1617-1740.
54. Foster, A. L., Petrochemistry Directs Natural-Gas Conversion at Lion Oil Co. Plant, Oil, and Gas Jour., vol. 45, June 22, 1946, pp. 98-103, 105.
55. Frey, F. E., Pyrolysis of Saturated Hydrocarbons: Ind. Eng. Chem., vol. 26, Feb. 1934, pp. 198-203.
56. Frolich, P. K. and Wiezevich, P. V., Cracking and Polymerization of Low-Molecular-Weight Hydrocarbons: Ind. Eng. Chem., vol. 27, Sept. 1935, pp. 1055-1062.
57. Gallie, J.F., Carbon Black: Petrol. Refiner, vol. 23, Mar. 1944, pp. 97-108; Apr. 1944, pp. 115-124.
58. Gallie, J. F., Carbon Black in its Relationship to the Natural Gas Industry: Gas Age, vol. 96, Sept. 6, 1945, pp. 43-48, 80; Gas, vol. 21, Sept. 1945, pp. 19-20; Interstate Oil Compact Quarterly Bulletin, vol. 4, Nos. 1 and 2, June 1945, pp. 135-146.
59. Hasche, R. Leonard, Acetylene Industry in Wartime Germany: Chem and Met. Eng., vol. 52, Oct. 1945, pp. 116-119; Chem. and Eng. News, vol. 23, Oct. 25, 1945, p. 1840.
60. Hessek, W. J., van Krevelen, D. W., and Waterman, H. L., Induced Pyrolysis of Methane: Soc. Chem. Ind. Jour., vol. 58, Nov. 1939, pp. 323-327.
61. Hurd, Charles D., The Pyrolysis of Carbon Compounds: Chem. Cat. Co., Inc., New York, 1929, 807 pp.
62. Komarewsky, V. L., and Reisz, C. H., Production of Butadiene by Single-Stage Dehydrogenation of Butane: Oil and Gas Jour., vol. 41, Sept. 17, 1942, pp. 33, 37, 39.

63. Lee, James A., Synthetic Ammonia Produced from Natural Gas: Chem. and Met. Eng., vol. 52, Dec. 1945, pp. 94-96.
64. Lowy, Alexander, Chart of Recent Aliphatic Chemicals: Ind. Eng. Chem., news ed., vol. 10, Jan. 10, 1932, p. 6.
65. Lowy, Alexander, Chart of Products Derived from Acetylene: Ind. Eng. Chem., news ed., vol. 11, May 20, 1933, p. 156.
66. Mitchell, Guy S., Ammonia - Its Production from Natural Gas: Petrol. Refiner, vol. 25, June 1946, pp. 97-111.
67. Nieuwland, Julius A. and Vogt, Richard R., The Chemistry of Acetylene, Reinhold Pub. Corp., New York, 1945, 219 pp.
68. Schoch, E. P., Natural Gas as the Raw Material for New Products. Use of Electric Discharges: Amer. Gas Jour., vol. 162, June 1945, pp. 11-14; Univ. of Texas Pub. No. 4503, Jan. 15, 1945, pp. 36-40.
69. Smith, H. M., Grandone, Peter, and Rall, H. T., The Production of Motor Fuels from Natural Gas. 1. Preliminary Report on the Pyrolysis of Methane: Bureau of Mines Report of Investigations 3143, Oct. 1931, 12 pp.
70. Teter, J. W., Olson, L. E., and Ries, H. E., Aliphatic Nitriles from Olefins and Ammonia: Paper presented before the Division of Petrol. Chem. of the Amer. Chem. Soc. -General Papers, Apr. 8-12, 1946, Atlantic City, N. J.
71. Thayer, C. H., Lassiat, R. C., and Lederer, E. R. Houdry Process Applied to the Manufacture of Butadiene: Petrol. Eng., vol. 14, Oct. 1942, pp. 29-30; Auto. Ind., vol. 87, Oct. 15, 1942, pp. 30-32; Rubber Age, vol. 52, Oct. 1942, pp. 39-41; Nat. Petrol. News vol. 34, Sept. 30, 1942, pp. R305-306; Mech. Eng., vol. 64, Nov. 1942, pp. 777-778; Chem. and Met. Eng., vol. 49, Nov. 1942, pp. 116-117.
72. Thornton, D. P., Jr., Fertilizer from Natural Gas: Nat. Petrol. News, vol. 38, July 3, 1946, pp. R483-488.
73. Tropsch, Hans, and Egloff, Gustav, High-Temperature Pyrolysis of Gaseous Paraffin Hydrocarbons: Ind. Eng. Chem., vol. 27, Sept. 1935, pp. 1063-1067.
74. Yeddanapolli, L. M., Decomposition of Methane in Glow Discharge at Liquid-Air Temperature: Jour. Chem. Phys., vol. 10, May 1942, pp. 249-260.

Oxidation

75. Ethyl Alcohol Made from Refinery Ethylene: Chem. and Met. Eng., vol. 52, Nov. 1945, pp. 96-98, 136-139.
76. New Markets: Chem. and Eng. News, vol. 23, Oct. 25, 1945, pp. 1911+.
77. Oil Company's Chemicals from Natural Gas Refinery Makes Formaldehyde, Methanol and Related Compounds: Nat. Petrol. News, vol. 35, Feb. 3, 1943, pp. R72-73.
78. Spirit of the Times; Ethyl and Other Alcohols from Petroleum: Petrol. Refiners, vol. 23, Jan. 1944, pp. 101-104.
79. Benson, G., New Process for Acetic Anhydride: Chem. and Met. Eng., vol. 47, Mar. 1940, pp. 150-151.
80. Brooks, Benjamin T., Synthetic Alcohols and Related Products from Petroleum. I. Olefin Raw Materials: Ind. Eng. Chem., vol. 27, Mar. 1935, pp. 278-282. II. Manufacture of Alcohols and Esters: Ibid., pp. 282-288.

81. Brooks, Benjamin T., and Ellis, Carleton, Alcohols and Related Products from Petroleum Olefins: The Science of Petrol., vol. 4, Oxford Univ. Press, London, 1938, pp. 2805-2811.

82. Daugherty, R. J., Chemicals, Solvents by Natural-Gas Oxidation: Oil and Gas Jour., vol. 41, Jan. 21, 1943, p. 36.

83. Egloff, Gustav, and Hulla, G., Conversion of Oxygen Derivatives of Hydrocarbons into Butadiene: Chem. Rev., vol. 36, Feb. 1945, pp. 63, 141.

84. Egloff, Gustav, Nordman, D. V., and Van Arsdell, P. M., The Oxidation of Aliphatic Hydrocarbons: Oil and Gas Jour., vol. 41, Sept. 24, 1942, pp. 207-210; Oct. 1, 1942, pp. 35-36; Oct. 8, 1942, pp. 49, 51-53.

85. Egloff, Gustav, and Schaad, R. E., The Oxidation of the Paraffin Hydrocarbons: Chem. Rev., vol. 6, March 1929, pp. 91-141.

86. Howes, D. A., The Synthesis of Methanol and Higher Alcohols from Water Gas: The Science of Petrol., vol. 4, Oxford Univ. Press, 1938, pp. 2812-2821.

87. Linford, Hooper, Chemical Utilization of Natural Gas and Gasoline Hydrocarbons by Oxidation: Petrol. Refiner, vol. 21, Dec. 1942, pp. 69-76; Nat. Petrol. News, vol. 35, Jan. 6, 1943, pp. R15-19; Calif. Oil World, vol. 35, Nov. 14, 1942, pp. 13-21; Petrol. Eng., vol. 14, Jan. 1943, pp. 89, 91-92, 94, 96, 98; (cond.) Oil and Gas Jour., vol. 41, Nov. 12, 1942, pp. 71, 73, 266.

88. McBee, E. T., Hass, H. B., and Wiseman, P. A., Catalytic Vapor-Phase Oxidation of Ethylene: Ind. Eng. Chem., vol. 37, May 1945, pp. 432-438.

89. Marek, L. F., and Hahn, Dorothy A., The Catalytic Oxidation of Organic Compounds in the Vapor Phase: Chem. Cat. Co., Inc., New York, 1932, 486 pp.

90. Reed, R. M., Commercial Production of Pure Hydrogen from Hydrocarbons and Steam: Am. Inst. Chem. Eng., Trans., vol. 41, Aug. 1945, pp. 453-462; Petrol. Refiner, vol. 24, Sept. 1945, pp. 119-122.

91. Taylor, R., Catalytic Production of Ethyl Alcohol from Ethylene: The Science of Petrol., vol. 4, Oxford Univ. Press, London, 1938, pp. 2802-2804.

92. Walker, J. Frederic, Formaldehyde: Reinhold Pub. Corp., New York, 1944, 397 pp.

93. Wiezevich, P. J., and Frolich, P. K., Direct Oxidation of Saturated Hydrocarbons at High Pressure: Ind. Eng. Chem., vol. 26, Mar. 1934, pp. 267-276.

Halogenation

94. Anantakrishman, S. V., and Venkataraman, R., The Reaction between Ethylene Derivatives and the Halogens: Chem. Rev., vol. 33, Aug. 1943, pp. 27-55.

95. Brooks, Benjamin T., Glycols and Related Compounds from Oil-Gas Olefines: The Science of Petrol., vol. 4, Oxford Univ. Press, London, 1938, pp. 2781-2786.

96. Egloff, Gustav, and Alexander, M., Halogenation of Aliphatic Hydrocarbons: Oil and Gas Jour., vol. 41, Aug. 20, 1942, pp. 41-42, 58-61; Aug. 27, 1942, pp. 39-40, 48; Sept. 3, 1942, pp. 34-37; Sept. 10, 1942, pp. 42, 44, 46.

97. Egloff, Gustav, Schaad, R. E., and Lowy, C. O., Jr., Halogenation of the Paraffin Hydrocarbons: Chem. Rev., vol. 8, Feb. 1931, pp. 1-80.

98. Finger, G. C., Fluorine Compounds in Organic Synthesis: Chem. and Met. Eng., vol. 51, June 1944, pp. 101-103.

99. Groll, H. P. A., and Hearne, G., Halogenation of Hydrocarbons; Substitution of Chlorine and Bromine into Straight-Chain Olefins: Ind. Eng. Chem., vol. 31, Dec. 1939, pp. 1530-1537.

100. Groll, H. P. A., Hearne, G., Rust, F. F., and Vaughan, W. E., Halogenation of Hydrocarbons; Chlorination of Olefins and Olefin-Paraffin Mixtures at Moderate Temperatures; Induced Substitutions: Ind. Eng. Chem., vol. 31, Oct. 1939, pp. 1239-1244.

101. Hadley, E. H., and Bigelow, L. A., Action of Elementary Fluorine upon Organic Compounds; The Vapor Phase Fluorination of Methane: Jour. Amer. Chem. Soc., vol. 62, Dec. 1940, pp. 3302-3303.

102. Hass, H. B., The Chlorination of Methane and Its Homologues: The Science of Petrol., vol. 4, Oxford Univ. Press, 1938, pp. 2787-2794.

103. Hass, H. B., The Addition of Halogens to Olefin Bonds: The Science of Petrol., vol. 4, Oxford Univ. Press, London, 1938, pp. 2777-2780.

104. Hass, H. B., McBee, E. T., and Weber, Paul, Syntheses from Natural-Gas Hydrocarbons. Identity of Monochlorides from Chlorination of Simpler Paraffins: Ind. Eng. Chem., vol. 27, Oct. 1935, pp. 1190-1195.

105. Hass, H. B., McBee, E. T., and Weber, Paul, Chlorination of Paraffins: Ind. Eng. Chem.; vol. 28, 1936, p. 333.

106. McBee, E. T., and Hass, H. B., Recent Progress in Chlorination, 1937-1940: Ind. Eng. Chem., vol. 33, Feb. 1941, pp. 137-142.

107. McBee, E. T., Hass, H. B., Neher, C. M., and Strickland, H. Chlorination of Methane: Ind. Eng. Chem., vol. 34, Mar. 1942, pp. 296-300.

108. McGovern, E. W., Chlorohydrocarbon Solvents: Ind. Eng. Chem., vol. 35, Dec. 1943, pp. 1230-1239.

109. Wiezevich, Peter J., and Vesterdal, Hans, G., Halogenated Hydrocarbon Solvents: Chem. Rev., vol. 19, Oct. 1936, pp. 101-117.

Nitrogen

110. Campbell, Arthur William, Nitroparaffins and Derivatives as Heat Sensitizers for Rubber Lattices: Ind. Eng. Chem., vol. 34, Sept. 1942, pp. 1106-1107.

111. Bogin, Charles, and Wampner, H. L., Nitroparaffins as Solvents in the Coating Industry: Ind. Eng. Chem. vol. 34, Sept. 1942, pp. 1091-1096.

112. Boyd, Thomas, and Hass, H. B., Nitration of Methane: Ind. Eng. Chem., vol. 34, Mar. 1942, pp. 300-304.

113. Egloff, Gustav, Alexander, M., and Van Arsdell, P. M., Nitration of Aliphatic Hydrocarbons: Oil and Gas Journal., vol. 41, Oct. 15, 1942, pp. 39-41, 44; Oct. 22, 1942, pp. 49, 51.

114. Ericsson, Ralph L., Solvent Uses of Nitroparaffins: Ind. Eng. Chem., vol. 35, Oct. 1943, pp. 1026-1030.

115. Hass, H. B., Recent Developments in Nitroparaffins: Ind. Eng. Chem., vol. 35, Nov. 1943, pp. 1146-1152.

116. Hass, H. B., Hodge, E. B., and Vanderbilt, B. M., Nitration of Gaseous Paraffins: Ind. Eng. Chem., vol. 28, Mar. 1936, pp. 339-344.

117. Hass, H. B., and Riley, Elizabeth F., The Nitroparaffins: Chem. Rev., vol. 32, June 1943, pp. 373-430.

118. Hibshman, H. J., Pierson, E. H., and Hass, H. B., Nitrogen of Ethane: Ind. Eng. Chem., vol. 32, Mar. 1940, pp. 427-429.

119. Hass, H. B., Dorsky, Julian, and Hodge, E. B., Nitration of Propane by Nitrogen Dioxide: Ind. Eng. Chem., vol. 33, Sept. 1941, pp. 1138-1143.

Sulfurization

120. Nat. Petrol. News, Socony-Vac Reports Cheaper Thiophene Process. Forecasts New Uses in Plastics and Dyes: Vol. 37, Jan. 31, 1945, p. 34; Chem. and Met. Eng., vol. 52, Mar. 1945, p. 138; Chem. Ind., vol. 56, Mar. 1945, p. 428+.

121. Bacon, R. F., and Boe, E. S., Hydrogen Sulfide Production for Sulfur and Hydrocarbons: Ind. Eng. Chem., vol. 37, May 1945, pp. 469-474.

122. Briscoe, H. V. A., Peel, J. B., and Robinson, P. L., Production of Thiophene by the Interaction of Acetylene and Carbon Disulphide: Chem. Soc. Jour., Nov. 1928, pp. 2857-2858.

123. Brooks, B. T., and Humphrey, I., The Action of Concentrated Sulfuric Acid on Olefins, with Particular Reference to the Refining of Petroleum Distillates: Jour. Amer. Chem. Soc., vol. 40, 1918, pp. 822-856.

124. Ellis, Carleton, Utilization of Sulfur Compounds: pp. 486-488; The Chemistry of Petroleum Derivatives, vol. II: Reinhold Pub. Corp., New York, 1937, 1464 pp.

125. Folkins, H. O., and Miller, E., Carbon Disulfide from Methane and Sulfur: (abs.) Nat. Petrol. News, vol. 37, Feb. 7, 1945, pt. 2, p. R132; Pure Oil News, vol. 27, 1944, p. 14.

126. Rasmussen, H. E., Hansford, R. C., and Sachanen, A. N., Reactions of Aliphatic Hydrocarbons with Sulfur; Production of Olefins, Diolefins, and Thiophene: Ind. Eng. Chem., vol. 38, Apr. 1946, pp. 376-382.

127. Thacker, C. M., and Miller, E., Carbon Disulfide Production: Effect of Catalysts on Reaction of Methane with Sulfur: Ind. Eng. Chem., vol. 36, Feb. 1944, pp. 182-184.

128. Waterman, H. I., and van Viodrop, C., Preparation of Carbon Disulphide from Methane and Hydrogen Sulphide: Soc. Chem. Ind. Jour., vol. 58, Mar. 1939, pp. 109-110.

Desulfurization

129. Byrnes, A. C., Bradley, W. E., and Lee, M. W., Catalytic Desulfurizatio of Petroleum Stocks by Cobalt Molybdate Process: Nat. Petrol. News, vol. 36, Feb. 2, 1944, pp. R102, R104, R106, R108, R110, R112-113.

130. Cooper, C. W., and Waddle, H. Recovery of Free Sulfur from Natural Gas: Gas, vol. 21, July 1945, pp. 31-33.

131. Guthrie, Boyd, and Simmons, M. C., Effects of Desulfurization on the Lead Susceptibility of Distillates from Some Crude Oils from Texas, New Mexico, and Oklahoma: Bureau of Mines Rept. of Investigations, 3729, Nov. 1943, 16 pp.; (cond.) Nat. Petrol. News, vol. 37, Apr. 4, 1945, pp. R309-312, R314-317.

132. Heineman, Heinz, Digest of United States Patents on Desulfurization: Petrol. Ref., vol. 23, June 1944, pp. 150, 152, 154, 156, 158, 160, 162, 166, 168.

133. Heineman, Heinz, Digest of United States Patents on Desulfurization Issued in 1944: Petrol. Ref., vol. 24, May 1945, pp. 196, 198, 200, 204, 208, 210.

134. Love, F. H., Desulphurization of Gas in the McKannie Field: Petrol. Eng., vol. 15, June 1944, pp. 55-58.

135. Reed, R. M., Desulfurization of Petroleum Hydrocarbons: Oil and Gas Jour., vol. 44, Mar. 30, 1946, pp. 219-220, 222-224, 226.

136. Ryan, J. G., Influence of Sulfur Compounds on Octane Number and Lead Susceptibility of Gasoline: Ind. Eng. Chem., vol. 34, July 1942, pp. 824-832.

137. Schulze, W. A., and Alden, R. C., Catalytic Desulfurization to Improve Aviation Blending Naphthas: Oil and Gas Jour., vol. 38, Nov. 17, 1939, pp. 199-200, 202-204; Ref. and Nat. Gaso. Mfg., vol. 18, Nov. 1939, pp. 96-99, 137.

Alkylation

138. Anhydrous Hydrofluoric Acid; Properties as an Alkylation Catalyst: Nat. Petrol. News., vol. 34, Oct. 28, 1942, pp. R366-368.

139. Alden, R. C., Frey, F. E., Hepp, H. J., and McReynolds, L. A., The Story of Diisopropyl: Oil and Gas Jour. vol. 44, Feb. 9, 1946, pp. 70-73, 103-104, 106-107.

140. Birch, S. F., Dustan, A. E., Fidler, F. A., Pim, F. B., and Tait, T., High-Octane Isoparaffinic Fuels; Production by the Addition of Olefins to Isoparaffins: Ind. Eng. Chem., vol. 31, July 1939, pp. 884-891.

141. Caesar, P. D., and Francis, A. W., Low-Temperature Catalytic Alkylation of Iso-Paraffins: Ind. Eng. Chem., vol. 33, Nov. 1941, pp. 1426-1428; (abs.) Nat. Petrol. News, vol. 33, Oct. 1, 1941, pp. R308+.

142. Egloff, Gustav, and Hulla, George, The Alkylation of Alkanes: Chem. Rev., vol. 37, Dec. 1945, pp. 323-399.

143. Clark, Melvin E., Neohexane for 100-Octane Plus: Chem. and Met. Eng., vol. 47, Apr. 1940, pp. 225-227.

144. Frey, F. E., and Hepp, J. H., Noncatalytic Addition of Ethylene to Paraffin Hydrocarbons: Ind. Eng. Chem., vol. 28, Dec. 1936, pp. 1439-1445.

145. Gerhold, C. G., and others, Development of the Hydrogen Fluoride Alkylation Process: Amer. Inst. Chem. Eng. Trans., vol. 39, Dec. 1943, pp. 793-810; Nat. Petrol. News, vol. 36, Mar. 1, 1944, pp. R146+; Petrol. Eng., vol. 15; Ref. Annual, July 1, 1944, pp. 256+.

146. Heineman, Heinz, Digest of United States Patents on Alkylation of Hydrocarbons: I. Petrol. Ref., vol. 21, Nov. 1942, pp. 176-178; II. Ibid., vol. 22, Aug. 1943, pp. 148, 150, 154, 156, 160; III. Ibid., vol. 23, May 1944, pp. 164, 168, 170, 172, 174; IV. Ibid. vol. 24, July 1945, pp. 170, 172, 174, 176-178, 180.

147. Linn, C. B., and Grosse, A. V., Alkylation of Isoparaffins by Olefins in Presence of Hydrogen Fluoride: Ind. Eng. Chem., vol. 37, Oct. 1945, pp. 924-929.

148. Oberfell, G. G., and Frey, F. E., Thermal Alkylation and Neohexane: Oil and Gas Jour., vol. 38, Nov. 23, 1939, pp. 50-51; Nov. 30, 1939, pp. 70, 73-74, 75; Amer. Petrol. Inst. Proc., vol. 20 (3) 1939, pp. 78-88; (cond.) Nat. Petrol. News, vol. 31, Nov. 29, 1939, pp. R502-503, R505-506, R508-509.

149. O'Kelly, A. A., and Sachanen, A. N., Alkylation of Paraffins in Presence of Homogeneous Catalysts; Synthesis of Neohexane and Triptane: Ind. Eng. Chem. vol. 38, May 1946, pp. 462-467.

150. Pardee, W. A., and Dodge, B. F., Catalytic Alkylation of Benzene with Ethylene: Ind. Eng. Chem., vol. 35, Mar. 1943, pp. 273-278; Nat. Petrol. News, vol. 35, Apr. 7, 1943, pp. R180-184.

151. Phillips Petroleum Co., Hydrofluoric Acid Alkylation: Phillips Petrol. Co., Chem. Prod. Dept., Bartlesville, Okla., 1946, 380 pp.

152. Pines, H., Grosse, A. V., and Ipatieff, V. N., Alkylation of Paraffins at Low Temperatures on the Presence of Aluminum Chloride: Jour. Amer. Chem. Soc., vol. 64, Jan. 1942, pp. 33-36.

153. Schmerling, Louis, The Mechanism of the Alkylation of Paraffins: Jour. Amer. Chem. Soc., vol. 67, Oct. 1945, pp. 1778-1783.

154. Weinrich, W., Alkylated Cresols from Refinery Gases: Ind. Eng. Chem., vol. 35, Mar. 1943, pp. 264-272.

Isomerization

155. New Process for Catalytic Conversion of Normal into Isobutane: Nat. Petrol. News, vol. 34, June 10, 1942, pp. R194-195.

156. Alden, R. C., Normal Butane Conversion: Nat. Petrol. News, vol. 35, May 5, 1943, pp. R222-224; Petrol. Ref., vol. 22, 1943, pp. 1457; Proc. NGAA 22d Annual Conv., Apr. 1943.

157. Chenicek, J. A., and others, Butane Isomerization; Universal Oil Products Co., Method Using Aluminum Chloride as Catalyst: Nat. Petrol. News, vol. 36, Oct. 4, 1944, pp. R678, R680-682.

158. Coulthrust, L. J., Shell Isomerization Process for Producing Isobutane: Nat. Petrol. News, vol. 33, Dec. 24, 1941, pp. R403-404, R406; Pet. Eng., vol. 13, Jan. 1942, pp. 113, 116+.

159. Egloff, Gustav, Hulla, George, and Komarewsky, V. I., Isomerization of Pure Hydrocarbons: Reinhold Pub. Corp., New York, 1942, 499 pp.

160. Evering, B. L., Fragen, N., and Weems, G. S., Commercial Isomerization of Lighter Paraffins: Oil and Gas Jour., vol. 43, Oct. 28, 1944, pp. 77, 81-82, 85-86; Nat. Petrol. News, vol. 36, Nov. 1, 1944, pp. R737-742; Chem. and Eng. News, vol. 22, Nov. 10, 1944, pp. 1898-1902; Petrol. Ref., vol. 23, Nov. 1944, pp. 91-105.

161. Foster, A. L., Isomerization, A Useful But As Yet A Little-Used Tool For the Refiner: Oil and Gas Jour., vol. 41, Feb. 25, 1943, pp. 66, 69, 71-72; Mar. 4, 1943, pp. 51-52.

162. Galstraun, L. S., Isopentane Produced by Liquid-Phase Isomerization: Chem. Met. Eng., vol. 52, Sept. 1945, pp. 109-111.

163. Heinemann, Heinz, Digest of United States Patents on Isomerization of Hydrocarbons: I. Petrol. Ref., vol. 21, Aug. 1942, pp. 136-139; II. Ibid., vol. 22, July 1943, pp. 126, 128, 130, 134; III. Ibid. vol. 23, Aug. 1944, pp. 154, 158, 160, 162, 166, 168; IV. Ibid., vol. 24, Nov. 1945, pp. 208, 210, 212, 214, 216, 217.

164. Murphy, George B., Catalytic Isomerization Will Put Nation Far in Lead in Aviation-Gasoline Supply: Nat. Petrol. News, vol. 33, Dec. 24, 1941, pp. R401-402.

165. Wilson, Edith, Isomerization of Hydrocarbons: Chem. Rev., vol. 21, Aug. 1937, pp. 129-167.

Hydrogenation

166. Brown, C. L., and Gohr, E. J., The Hydrogenation of Olefin Polymers for the Manufacture of High-Octane-Number Fuels: Proc., Second World Petrol. Cong., Paris, 1937, vol. 2, pp. 289-298.

167. Heinemann, Heinz, Digest of United States Patents on Catalytic Hydrogenation of Hydrocarbons: Petrol. Ref., vol. 23, Jan. 1944, pp. 154, 156, 158, 160, 164.

168. Heinemann, Heinz, Digest of United States Patents on Hydrogenation and Halogenation: Petrol. Ref., vol. 23, Nov. 1944, pp. 182, 186, 190, 192, 194.

169. Murphree, E. V., Brown, C. L., and Gohr, E. J., Hydrogenation of Petroleum: Ind. Eng. Chem., vol. 32, Sept. 1940, pp. 1203-1212.

170. Stengel, L. A., and Shreve, R. N., Economic Aspects: Ind. Eng. Chem., vol. 32, Sept. 1940, pp. 1212-1215.

Dehydrogenation

171. Frey, F. E., and Huppke, W. F., Equilibrium Dehydrogenation of Ethane, Propane and the Butanes: Ind. Eng. Chem., vol. 25, Jan. 1933, pp. 54-59.

172. Grosse, A. V., and others, Catalytic Dehydrogenation Process (Gaseous Paraffins to Olefins): Amer. Petrol. Inst. Proc., vol. 20, (3), 1939, pp. 110-120; Oil and Gas Jour., vol. 38, Nov. 23, 1939, pp. 53, 55-56; (cond.) Nat. Petrol. News, vol. 31, Nov. 29, 1939, pp. R520-521.

173. Grosse, A. V., and Ipatieff, V. N., Catalytic Dehydrogenation of Gaseous Paraffins: Ind. Eng. Chem., vol. 32, Feb. 1940, pp. 268-272.

174. Heinemann, Heinz, Digest of United States Patents on Dehydrogenation and Dehydrohalogenation of Hydrocarbons: Petrol. Ref., vol. 23, Apr. 1944, pp. 142, 146, 148, 150, 152, 154.

175. Heinemann, Heinz, Digest of United States Patents on Hydrogenation and Dehydrogenation of Hydrocarbons: Petrol. Ref., vol. 24, June 1945, pp. 170, 172, 174, 178, 180.

176. Lassiat, R. C., and Parker, F. D., Butane Dehydrogenation by the Houdry Process: Oil and Gas Jour., vol. 43, Nov. 18, 1944, pp. 229+; Petrol. Ref., vol. 23, Nov. 1944, pp. 85-90; Nat Petrol. News, vol. 36, Dec. 6, 1944, pp. R842-847.

177. Riesz, C. H., and others, Catalytic Dehydrogenation of Natural Gas Hydrocarbons: Oil and Gas Jour., vol. 43, July 15, 1944, pp. 67-69+.

178. Watson, C. C., and others, Butane Dehydrogenation: Amer. Inst. Chem. Eng. Trans., vol. 40, June 1944, pp. 309-315; Nat. Petrol. News, vol. 36, Aug. 2, 1944, pp. R509-510.

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Polymerization

179. Catalytic Refining Methods: Oil and Gas Jour., vol. 37, Mar. 30, 1939, pp. 86, 88, 91, 93.

180. Bogk, J. E., Ostergaard, P., and Smoley, E. R., Naphtha Polyform and Gas Reversion Processes: Amer. Petrol. Inst. Proc., vol. 21, sec. III, Nov. 1940, pp. 17-36; (excerpt) Oil and Gas Jour., vol. 39, Dec. 19, 1940, pp. 43-44, 47+.

181. Burk, Robert E., Thompson, Howard E., Weith, Archie J., and Williams, Ira, Polymerization and Its Applications in the Fields of Rubber, Synthetic Resins, and Petroleum: Reinhold Pub. Corp., New York, 1937, 312 pp.

182. Carothers, Wallace H., Polymerization: Chem. Rev., vol. 8, June 1931, pp. 353-426.

183. Egloff, Gustav, Morrell, J. C., and Nelson, Edwin F., Motor Fuels from Polymerization: Ref. and Nat Gaso. Mfg., vol. 16, Nov. 1937, pp. 497+.

184. Ellis, Carleton, Tailoring the Long Molecule-Plastics: Ind. Eng. Chem., vol. 28, Oct. 1936, pp. 1130-1144.

185. Frey, F. E., and Hepp, H. J., Motor-Fuel Iso-paraffins by Thermal Gas Polymerization: Oil and Gas Jour., vol. 35, Jan. 7, 1937, pp. 40, 43, 46, 49.

186. Heinemann, Heinz, Digest of United States Patents; Polymerization of Hydrocarbons: Petrol. Ref., vol. 23, Feb. 1944, pp. 142, 144, 146, 148.

187. Heinemann, Heinz, Digest of United States Patents on Polymerization of Hydrocarbons: Petrol. Ref., vol. 24, Mar. 1945, pp. 178, 182, 184, 186.

188. Ipatieff, V. N., Catalytic Polymerization of Gaseous Olefins by Liquid Phosphoric Acid; I. Propylene: Ind. Eng. Chem., vol. 27, Sept. 1935, pp. 1067-1069.

189. Ipatieff, V. N., and Corson, B. B., Catalytic Polymerization of Gaseous Olefins by Liquid Phosphoric Acid; II Butylenes: Ind. Eng. Chem., vol. 27, Sept. 1935, pp. 1069-1071.

190. Keith, P. C., Jr., and Ward, J. T., The Thermal Conversion of Low Molecular-Weight Hydrocarbons to Motor Fuels: Chem. and Ind., vol. 27, July 3, 1936, pp. 532-538.

191. McAllister, S. H., The Catalytic Polymerization of Butylenes by Sulfuric Acid: Ref. and Nat Gaso. Mfg., vol. 16, Nov. 1937.

192. Ostergaard, Povl, and Smoley, Eugene R., Gulf Polyform Process: Ref. and Nat. Gaso. Mfg., vol. 19, Sept. 1940, pp. 67-78; Nat. Petrol. News, vol. 32, Sept. 18, 1940, pp. R330-331, R333-334, R336, R337, R340, R342, R344, R346-347.

193. Ridgway, C. M. and Maschwitz, P. A., New Thermal Polymerization Unit Installed by Pure Oil: Oil and Gas Jour., vol. 40, Oct. 30, 1941, pp. 30-31, 33, 48.

194. Ridgway, C. M., Wagner, C. R., and Swanson, H. R., Products of Polymerization: Nat. Petrol. News, vol. 28, Nov. 4, 1936, pp. 47-48, 50-52, 54-55.

195. Wagner, C. R., Production of Gasoline by Polymerization of Olefins: Ind. Eng. Chem., vol. 27, Aug. 1935, pp. 933-936.

Cyclization and Aromatization

196. Cadman, W. H., Thermal Treatment of Gaseous Hydrocarbons; II. Semi-Industrial Production of Aromatic Hydrocarbons from Natural Gas in Persia: Ind. Eng. Chem., vol. 26, Mar. 1934, pp. 315-320.
197. Grosse, A. V., Morrell, J. C., and Mattox, W. M., Catalytic Cyclization of Aliphatic Hydrocarbons to Aromatics: Ind. Eng. Chem., vol. 32, Apr. 1940, pp. 528-531.
198. Heinemann, Heinz, Digest of Patents on Catalytic Aromatization and Cyclization: Petrol. Ref., vol. 23, Oct. 1944, pp. 176, 178, 180, 182, 184.
199. Smith, D. J., and Moore, L. W., First Commercial Hydroforming Plant Now in Operation: Oil and Gas Jour., vol. 39, Mar. 27, 1941, pp. 87-88; Nat. Petrol. News, vol. 33, Apr. 2, 1941, pp. R98-100, 102; Petrol. Eng., vol. 12, Apr. 1941, pp. 23-24.
200. Trusty, A. W., Petroleum as a Source of the Aromatic Hydrocarbons: Petrol. Ref., vol. 22, Apr. 1943, pp. 83-87.

Hydrocarbon Synthesis

201. Alden, R. C., Conversion of Dry Natural Gas to Liquid Fuels: World Petrol., vol. 17, April 1946, pp. 46-49, 70.
202. Cipolon, Frank, "Synthetic" Natural Gas from Coal: Amer. Gas Jour., vol. 162, 1945, p. 60.
203. Cotton, Ernest, Germany's Fischer-Tropsch Process: Natural Petrol. News, vol. 38, June 5, 1946, pp. R425-426, 430, 432-434.
204. Egloff, Gustav, Nelson, E. F., and Morrell, J. C., Motor Fuel from Oil Cracking; Production by the Catalytic Water-Gas Reaction: Ind. Eng. Chem., vol. 29, May 1937, pp. 555-559.
205. Faragher, Warren F., Germans Made High Aromatic Aviation Gasoline by Coal Hydrogenation: Nat. Petrol. News, vol. 37, Nov. 7, 1945, pp. R851-855.
206. Fieldner, Arno C., and Fisher, Paul L., Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels from Oil Shale, Coal, Lignite, and Natural Gas: Bureau of Mines Inf. Circ. 7304, Jan. 1945, 18 pp.
207. Fieldner, Arno C., Storch, Henry H., and Hirst, Lester L., Bureau of Mines Research on the Hydrogenation and Liquefaction of Coal and Lignite: Bureau of Mines Tech. Paper 666, 1944, 69 pp.
208. Fischer, Fray, Roelen, Otto, and Feist W., The Synthesis of Gasoline by the Fischer-Tropsch Process (Translation): Petrol. Ref., vol. 22, Dec. 1943, pp. 97-104.
209. Fischer, Fray, Synthesis of Gasoline from Carbon Monoxide and Hydrogen at Atmospheric Pressure (Translation): Petrol. Ref., vol. 23, Feb. 1944, pp. 112-118.
210. Gordon, A. S., Uncatalyzed Reaction of Natural Gas and Steam: Ind. Eng. Chem. vol. 38, July 1946, pp. 718-720.
211. Keith, P. C., Gasoline from Natural Gas: Oil and Gas Jour., vol 45, June 15, 1946, pp. 102, 105, 107-108, 111-112; Amer. Gas Assoc. Monthly, vol. 28, June 1946, pp. 253-257, 296-297; Amer. Gas Jour., vol. 164, June 1946, pp. 11-15; Nat. Petrol. News, vol. 38, July 3, 1946, pp. R506-509, 511.

212. Komarewsky, V. I., Production of Synthetic Liquid Fuel from Natural Gas: Petrol. Ref., vol. 24, May 1945, pp. 96-98; Petrol. Eng., vol. 16, Aug. 1945, pp. 202, 204, 206.

213. Komarewsky, V. L., and Riesz, C. H., Fischer-Tropsch Synthesis and the Gas Industry: Petrol. Ref., vol. 23, Nov. 1944, pp. 91-98.

214. Morrison, G. O., Recent Developments at Shawinigas Chemicals, Ltd.: Chem. and Ind., vol. 60, May 24, 1941, pp. 387-392.

215. Ryan, Paul, Synthol Process for Manufacturing Liquid Hydrocarbons and Other Products from Natural Gas: Nat. Petrol. News, vol. 37, Apr. 1, 1945, pp. 36-38; Chem. and Ind., vol. 56, May 1945, p. 783; Petrol. Ref., vol. 24, Apr. 1945, p. 130; Gas Age, vol. 95, May 17, 1945, pp. 18-19; Oil and Gas Jour., vol. 43, Mar. 31, 1945, pp. 264-268; Gas, vol. 21, July 1945, p. 30.

216. Storch, H. H., Catalyst in Synthetic Liquid Fuel Processes: (abs) Oil and Gas Jour., vol. 43, Sept. 16, 1944, p. 103; (abs.) Petrol. Ref., vol. 23, Sept. 1944, pp. 144-146; Ind. Eng. Chem., vol. 37, Apr. 1945, pp. 340-351.

217. Underwood, A. J. V., Industrial Synthesis of Hydrocarbons from Hydrogen and Carbon Monoxide: Ind. Eng. Chem., vol. 32, Apr. 1940, pp. 449-454.

218. Wilcox, O. W., Synthetic Gasoline from Natural Gas: World Petrol., vol. 16, An. Ref. Issue, 1945, pp. 103-104, 120.